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著者(和文)	原亨和
Author(English)	MICHIKAZU HARA
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SURFACE CHEMISTRY ON ALUMINUM (111) SINGLE CRYSTAL

Hirose and Domen lab.
Michikazu Hara

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1. General Introduction.

1-1. The Surface Science of Non-Transition Metals

Various phenomena occur at boundaries among materials. The study of boundary or interface science has extended into many fields, especially, the study of solid surface has remarkably developed since the Second World War. The rise of electronics and construction technology has benefited the remarkable progress of this field after 1960's. Now, solid surface is studied in basic aspect such as the characteristic of material, structure and reaction and in applied aspect such as catalyst, semiconductor, new novel material production and so on.

The adsorption, reaction and desorption through solid metal surfaces are topics in subject of basic and applied research. Particularly, the phenomena on transition metal surfaces have long been studied in detail because of the high reactivity and a tremendous volume of basic results, which has been contributed to the development of surface analytical techniques, has been accumulated. Although we tend to imagine that atoms and molecules on a solid surface are rigidly fixed , these accumulated data revealed that they actually move around and thus the surface is fluid in so many word. For example, the reconstruction of the surface structure due to adsorbed species is common by accepted concept.[1] By now, basic results are sufficiently obtained. The surface science of transition metals faces new problems.

The chemistry of non-transition metal or sp-metal as much as the chemistry of transition metal has been studied in many fields. Non-transition metals which does not contain the occupied d-orbitals in valence orbitals show different reactivities from transition metals because d-electron in transition metals concern many reactions such as back donation or dissociative reaction. In organo metallic chemistry, non-transition metals form stable metal-carbon bond and produce alkyl-metallic compounds which have played an important role in industry.

The surface science of non-transition metals has also been studied for a long time and offered enormous informations to us. However the number of studies of the adsorption, reaction and desorption on non-transition metal surfaces are much lower than that of transition metals. This is because the surfaces of non-transition metals not to have effective d-electron, on which the adsorption of carbon monoxide by back donation or the dissociative adsorption of hydrogen molecule can not take place, may be misunderstood as having as poor reactivity and thus as the surfaces with less interesting subject for surface reactions. As a result, in the studies for the reactions between adsorbate and non-transition metal surfaces, high reactivity systems such as the adsorptions of oxygen or water on Al surfaces or the dry etching process which support the today prosperity of electronic industry have extensively been investigated although there are many interesting subjects in the reactions of non-transition metals.

Recently, the surface reactions of non-transition metals have been investigated under ultrahigh vacuum at the view point of organometallic chemistry.[2,3] It is well known in organometallic chemistry that non-transition metals such as Mg, Al and Zn react directly with alkylhalides (RX) to form alkylaluminumseskihalides like $R_3Al_2X_3$, RMgX or RZnX. The reaction between Mg and RX leads to the Grignard Reagent. The organometallic compounds such as the Grignard Reagents and alkylaluminumseskihalides are actually synthesized at a solid-liquid interface. Because there is virtually no method which can directly investigate the phenomena on these interfaces, it is not clear how these organometallic compounds are formed on the interfaces. Therefore the surface analytical techniques under ultrahigh vacuum are hopeful about the direct observations of the interface reactions. The study of the reaction between CH_3Br at Mg atom on a Mg single crystal (0001) surface revealed that CH_3Br molecules undergo decomposition on adsorption at such low temperature as 123 K leading the facile production of surface bromide (Mg-Br) accompanying the formation of gaseous ethane.[2] Electron spectroscopies of CH_3I molecules adsorbed on an Al surface revealed that adsorbed CH_3I was decomposed on the surface at 150 K giving the formations of a methylidyne group (C-H) and an Al-I bond.[3] These studies showed that methyl halides decomposed when they were adsorbed on the surfaces at low temperatures. The breakups of the carbon-halogen bond and the carbon-hydrogen bond at low temperatures are indicative of the extremely high reactivities of these non-transition metal surfaces to methyl halides. Although these pioneering studies proved for the first time the occurrence of decomposition of methyl halides on the non-transition metal surfaces, these reaction systems were too complex for surface analytical techniques to enable us to get at clear interpretations of the phenomena.

Actually these aimed at detecting the formation of organometallic compounds on non-transition metal surfaces although the formation itself could not be observed.

1-2. The desorptions of aluminum compounds by the reaction between adsorbate and Al surfaces.

Domen et al. found out the desorption of ethylene at low temperatures below 200 K from a CH_2I_2 adsorbed polycrystalline Al surface under ultrahigh vacuum.[4] This experiment was not begun with relation to organometallic chemistry at the beginning but relation to the laser desorption of CH_2I_2 on metal surfaces. This reaction have a close similarity to the Simmons-Smith reaction which generates a carbene ($:CH_2$) through an organozinc compound formed by the reaction between Zn and CH_2I_2.[5] Without alkene, the Simmons-Smith reaction produces ethylene by the coupling of carbenes and the behavior of the solid-liquid interface has not been cleared yet. As a result, an organoaluminum compound is expected to participate in the reaction on the surface.

So we investigated the CH_2I_2 adsorbed Al(111) surface under ultrahigh vacuum in order to understand the reaction of organo non-transition metal chemistry on the interface.[6] The experiment under ultrahigh vacuum means investigating the behavior on atomically clean surface to add to using electron spectroscopies as mentioned before. Usually, single crystal surfaces are used to make the interpretation for the behavior simple because it is possible that surface reaction depends greatly on surface structure and is often complex on polycrystalline surfaces. We found out the desorption of an organoaluminum compound from the CH_2I_2 adsorbed Al(111) surface in this study. This organoaluminum compound is composed of methyl group, hydrogen and iodine. To our knowledge, this is the first direct observation of an organometallic compound produced by a reaction between an adsorbate and a solid surface. This phenomenon revealed Al surface to have the aspect which differs entirely from transition metal surfaces. Transition metal surfaces such as Pt and Ni decompose hydrocarbon halides into surface alkyl groups (R-M) and surface halides (X-M).[7,8] Although hydrocarbons by coupling or hydrogenation of the surface alkyl group desorb from these surfaces, organometallic compound does not desorb.

On the CH_2I_2 adsorbed Al(111) surface, the organoaluminum compound and hydrogen molecule desorbs simultaneously at around 470 K.[9] The desorption of hydrogen from the surface is attributed to aluminum-hydrogen bond on the surface and takes place at higher temperature compared with the hydrogen desorption from general hydrogen adsorbed metal surfaces, on which hydrogen desorbs by the recombination of adsorbed hydrogen atom (hydrogen adatom) at around 300 K. To investigate this phenomenon, the experiment for a hydrogen adsorbed Al(111) surface was performed. Surprisingly, an aluminum hydride desorbed from the hydrogen adsorbed Al(111) surface.[10] The mass spectroscopy for the desorbed species was indicative of the desorption of the aluminum hydride such as AlH_3 (alane) or Al_2H_6 (dialane). In general, it is common sense that hydrogen molecule desorbs from hydrogen adsorbed metal surfaces. Although several studies for hydrogen adsorbed Al surfaces, that is to say, the simplest atom on the simplest sp-metal, have already been reported,[11,12,13] the desorption of the aluminum hydride has been overlooked because of this common sense which has been recognized on transition metal surfaces. Later, Kondoh et al. and Winkler et al. confirmed the desorption of aluminum hydride from hydrogen adsorbed Al(111), Al(110) and Al(100) surfaces and discussed that the formation and desorption of aluminum hydride depended sensitively on the surface structure.[14,15]

The formations and desorptions of organometallic compound or metal hydride by the reactions between the metal atoms at metal surfaces and adsorbates have never been observed in surface science. These phenomena mentioned above present us a basic problem, that is, why the surface Al atoms as organoaluminum compound or aluminum hydride desorb from the Al surface by the reactions between CH_2I_2 or hydrogen atom and the Al atom on the surface. The desorptions of these aluminum compounds need a driving force which breaks the Al-Al metallic bond among Al atoms on the surface and near surface. Surface chemistry of dry etching processes deals with the desorption of metal compound by the reaction between adsorbates and surface metal atoms and has remarkably progressed with the demand of VLSI technology.[9] The basic idea of a dry etching process then is to stimulate a surface reaction that will form a volatile compound which can be easily removed from the surface and pumped away. To date, the silicon/halogen system and aluminum/halogen are the most extensively characterized system in dry etching processes. In a dry etching process by the reaction between Al surface and Cl_2, the Al surface reacting with Cl_2 at room temperature results in isotropic etching by the desorptions of $AlCl_3$ and Al_2Cl_6.[16] These studies did not investigate the mechanism of the reaction but the reactivities between the Al surface and chlorine species (Cl_2 molecule, Cl atom and so on). This is because etching technology has been driven by manufacturing needs, but fundamental understanding of the gas phase and surface chemistry involved has lagged far behind.

As a result, there is no direct key, which can explain the formations and desorptions of the organoaluminum compound and aluminum hydride on the Al surfaces, in the accumulated results. The key is likely to exist in essential qualities of electropositive Al as an element, the chemical characters of Al and surface structure. The surface chemistry for the CH_2I_2 or hydrogen adsorbed Al(111) surface might lead to understanding the desorptions of metal compounds by the interface reactions on solid-gas phase or solid-liquid. Furthermore, investigating these phenomena on the Al surfaces, which do not obey the common sense in transition metal surfaces, would lead to understanding the characteristics of Al as a non-transition metal at a different viewpoint.

In this study, the formations and desorptions of aluminum compounds by the reactions between adsorbates and Al atoms on the Al surfaces through the hydrogen adsorbed Al(111) surface and CH_2I_2 adsorbed Al(111) surface were investigated under ultrahigh vacuum. This study reveals that the desorptions of aluminum compounds from the surfaces are due to the characteristics of Al as surface and a element and the surface chemistry of non-transition metals has completely different aspects from that of transition metals.

1-3. Contents

This paper is constructed by consists of eight sections. The summary of the contents from section 2 to 8 are given below:

Section 2.
Experimental.

There are many curious-looking methods and apparatus in ultrahigh vacuum (UHV) system. In this section, the significance for performing this study under UHV, UHV apparatus and surface analytical techniques are mentioned. Especially, because the preparation and cleaning for the Al(111) single crystal surface always annoyed me, I would like to mention that precisely.

Section 3.
Surface Reaction of CH_2I_2 with an Al(111) surface.

All of this study began at this system. In this section, the reactivity of CH_2I_2 with the Al(111) surface, the assignment of desorbed species from the surface and the reaction due to the organoaluminum compound, which is the ethylene formation, are mentioned. The formation and desorption of the organoaluminum compound and ethylene are discussed. This section contains the contents of the following papers:

Observation of an Alkyl Aluminum Complex formed by Reaction of CH_2I_2 with an Al(111) Surface.
M.Hara, K.Domen, M.Kato, T.Onishi
and H.Nozoye.
Chem. Comm. 1990, 23, 1717.

Surface Reaction of CH_2I_2 with an Al(111) Surface.
M.Hara, K.Domen, T.Onishi
and H.Nozoye.
J. Phys. Chem. in press.

Section 4.

The Desorption of Aluminum Hydride from a Hydrogen Adsorbed Al(111) Surface.

Generally, the desorption of hydrogen from hydrogen adsorbed metal surfaces obeys a rule due to kinetics. The observations by means of mass spectroscopy have ever asserted the hydrogen desorption from hydrogen adsorbed Al surfaces not to obey this rule. We found out the desorption of an aluminum hydride from the hydrogen adsorbed Al(111) surface. Thermal desorption experiments revealed the mass signal which have ever been regarded as hydrogen molecule to result from the mass fragmentation of the desorbed aluminum hydride. The desorption manner of aluminum hydride and the assignment of the desorbed aluminum hydride are described in this section. Furthermore, the formation of aluminum hydride on the surface was investigated by means of a photoelectron spectroscopy. This section contains the contents of the following papers:

Desorption of Aluminum Hydride from Hydrogen Adsorbed Al(111) Surface.
M.Hara, K.Domen, T.Onishi
and H.Nozoye.
J. Phys. Chem. 1991, 95, 6.

Formation and Desorption of Aluminum Hydride from Hydrogen Adsorbed Aluminum Surfaces.
M.Hara, K.Domen, T.Onishi
and H.Nozoye.
Surface Science 1991, 242, 459.

Section 5.

The Formation and Desorption Mechanism of Aluminum Hydride on Hydrogen Adsorbed Al(111) Surface.

By only kinetics, the behavior on surfaces can not be understood. The electronic structure and surface species of the hydrogen adsorbed Al(111) surface was observed by means of mainly ultraviolet photoelectron spectroscopy (UPS) and high resolution electron energy loss spectroscopy (HREELS). In section 4, the change of Al-H bond with increasing surface temperature and the drastic change of adsorbate at the desorption temperature of aluminum hydride are mentioned. These surface species changes are discussed with the help of the first-principles (ab initio) calculations. This section contains the contents of a following paper:

Electronic Structure of Hydrogen Adsorbed Al(111) Surface:
The Mechanism for The Formation of Aluminum Hydride.
M.Hara, K.Domen, C.Hirose,
H.Kondoh, C.Nishihara and H.Nozoye.
J. Chem. Phys. To be published.

Section 6.

Etching of Aluminum Surface by Hydrogen Atom.

The desorption of aluminum hydride leads to a dry etching process. The desorption of aluminum hydride from a thin Al film deposited on a Mo(111) single crystal surface was investigated. The availability of the dry etching process by the reaction between Al surfaces and hydrogen atom is indicated in this section. Section 6 contains the contents of a following paper:

Etching of Aluminum Film by Hydrogen Atoms.
M.Hara, K.Domen, T.Onishi
and H.Nozoye.
Appl. Phys. Lett. 1991, 14, 1793.

Section 7.
Summary.

I would like to summarize the desorptions of aluminum compounds by the reactions between adsorbates and Al surfaces with the help of all of results.

Section 8.
Ackowledgments.

The proverb that a nod is as good as a wink to a blind horse, all of people which have taken care of me must remember for me. I thank them in this section.

The other papers, which can not be contained in this paper, are as follows:

A HREELS Study on Hydrogen Adsorbed Al(111) surface.

H.Kondoh, C.Nishihara, H.Nozoye,

M.Hara and K.Domen.

Chem. Phys. Lett. in press.

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16. Mayer,T.M.;Amenn,M.S.;Vitkavage,D.J., Surface Chemistry of Dry Etching Process, in:THE CHEMICAL PHYSICS OF SOLID SURFACES AND HETEROGENIOUS CATALYSIS,Vol.5, Eds. King.D.A. ;Woodruff,D.P.;Springer:New York,1985.

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2. Experimental.

2-1. Ultrahigh vacuum (UHV) system.

In this study, the behaviors on the single crystal were investigated surface under UHV. It is not too much to say that the progress of surface science has been accompanied by the development of UHV technology. Firstly, UHV can realize the preparation and keeping of atomically clean surface. Al surfaces are oxidized by a little oxygen or water because of high electropositivity of Al. As a result, to investigate the behaviors on metallic Al surfaces, preparing atomically clean Al surfaces is demanded under the condition which makes oxygen or water exist hardly. UHV system can the most easily accomplish this condition. Next, various apparatus for surface analysis and operations can effectively be used under UHV. Because all of UHV apparatus such as BA-gauge, electron gun, ion sputter gun, mass spectrometer, X-ray source and so on are based on the occurrence of hot electron by hot filaments and the acceleration of hot electron, high vacuum is demanded to use these apparatus. Furthermore the life of these apparatus and the ability of analysis increase with decreasing base pressure.

Single crystal surfaces are frequently used in surface science. This is because single crystal surface has well-defined and uniform structure. Because the behavior of an adsorbate is liable to depend on the surface structures, the results and interpretations for the polycrystalline surface are often complex. Therefore single crystal surfaces are used to simplify the system. An Al(111) surface is the most close-packed and basic surface among the surfaces of f.c.c Al single crystal.

Thus, single crystal surfaces under UHV would be recognized to be the simplest systems.

2-2. UHV apparatus.

Several complex systems maintain simple UHV system. This study was carried out in two UHV systems.

A stainless-steel UHV chamber A is shown in Figure 1. A 500 $dm^3 s^{-1}$ turbo molecular pump (TMP) keeps the typical base pressure lower than 2 x 10^{-10} torr. There are two gas introduction systems in this chamber. the introduction system 1 lead to a gas doser in the chamber (see below). The gas introduction system 2 is used to introduce permanent gas such as H_2 and Ar for Ar^+ bombardment.

Figure 2 shows the analysis system in the chamber A. This chamber is equipped with an ion gun for Ar^+ bombardment, an electron gun, a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), a four-grid low energy electron diffraction (LEED) optics and a quadrupole mass spectrometer (m/e = 0 ~ 360) for thermal desorption spectroscopy (TDS). A gas doser is used to discharge molecular adsorbate into surface and is divided by a glass microchannel plate. Vapor from liquid sample or gas whose pressure is reduced to 10^{-5} ~

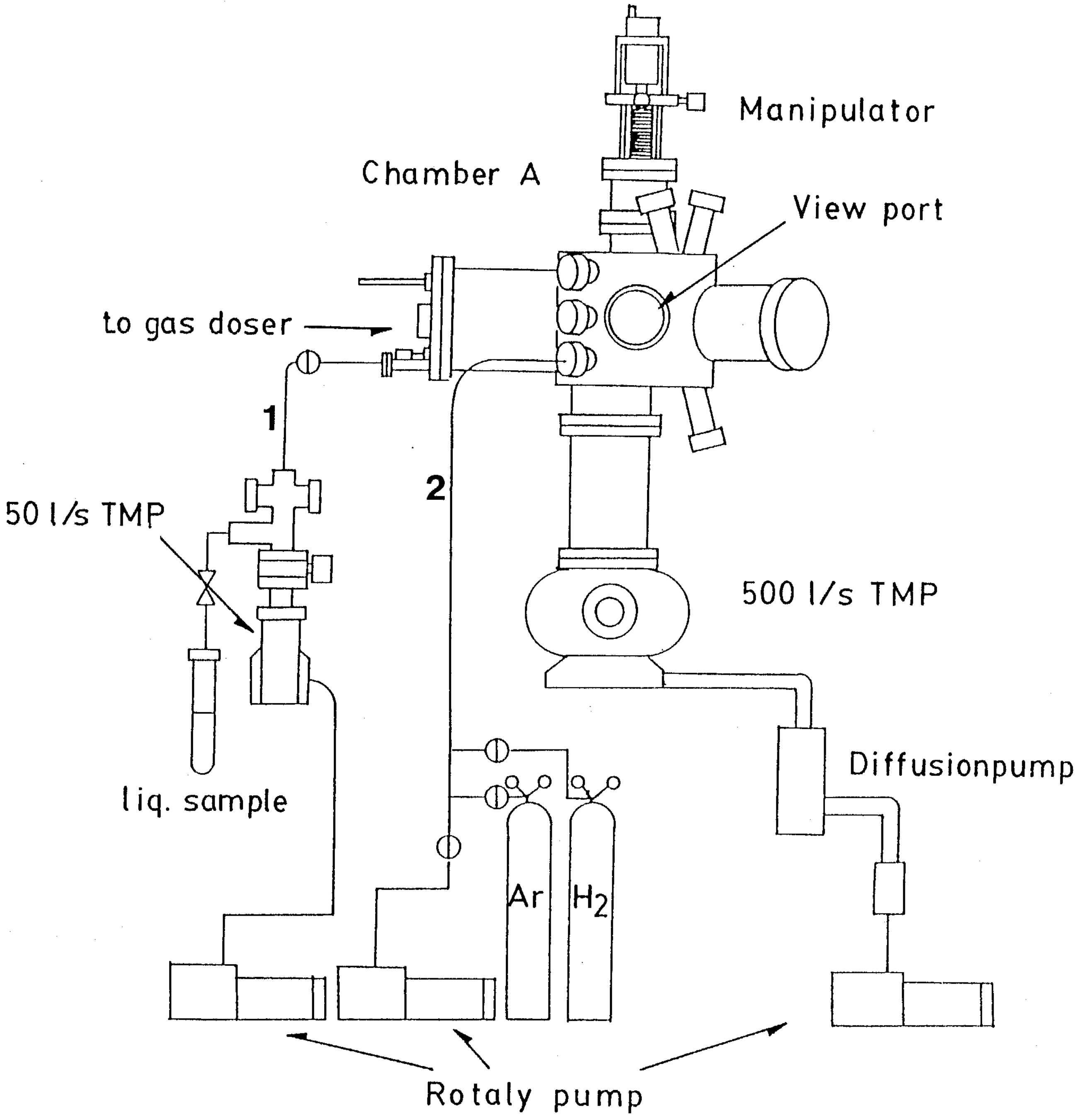


Figure 1. The UHV system on the chamber A.

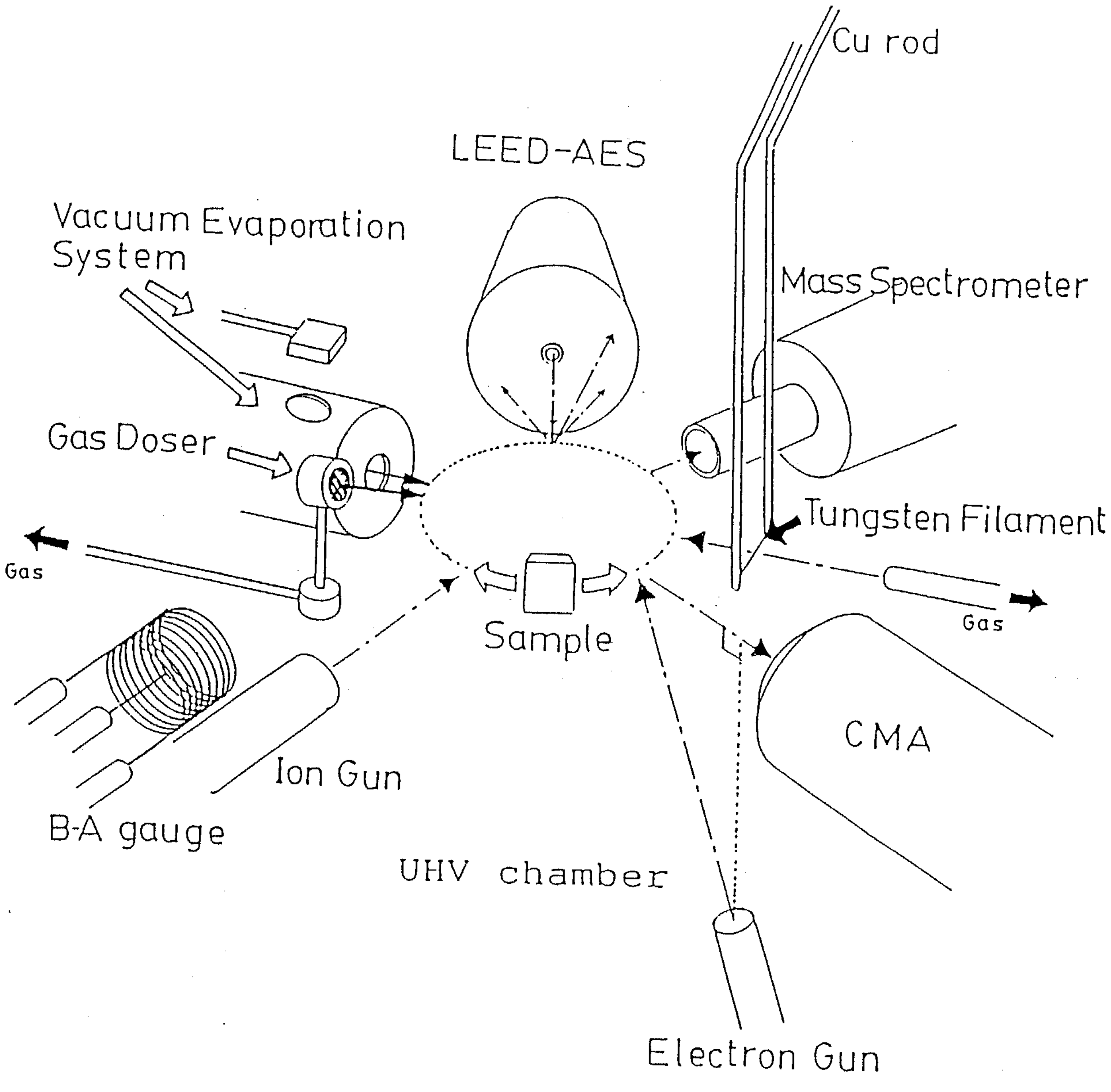


Figure 2. The UHV apparatus in the chamber A.

10^{-3} torr by an another evacuation system (50 dm^3s^{-1} TMP) outside UHV system becomes the molecular flux of $10^{-10} \sim 10^{-8}$ torr in UHV system through the glass microchannel plate of the gas doser. Subsequently, the surface is exposed to this molecular flux as beam. The adsorption by low pressure molecular flux means keeping UHV and prevent gas or vapor from contaminating UHV apparatus when adsorbate is introduced in UHV system. There is a tungsten filament for the generation of hydrogen atom in this chamber. The dissociative adsorption of hydrogen molecules can not take place on Al surfaces. Therefore in the experiments of the hydrogen adsorbed Al(111) surface, the adsorption of hydrogen atom was carried out by exposing the Al surface to hydrogen atoms which were produced by the thermal decomposition of hydrogen molecules by means of a hot tungsten filament. Rotating the sample on the circle shown in Figure 1 can perform various operations and measurements for the sample.

Figure 3 displays a chamber B. This chamber is made from demagnetic μ -metal and is based on a VG scientific ESCA LAB. MarkII . The chamber B is composed of an analysis chamber and a preparation chamber. Each chambers which have a pumping system composed of a 150 dm^3s^{-1} oil diffusion pump, an ion pump and a titanium sublimation pump assure UHV lower than 4 x 10^{-11} torr. The inside analysis chamber is shown in Figure 4. All of experiments were performed in the analysis chamber. There are the operational UHV apparatus of an ion gun for Ar^+

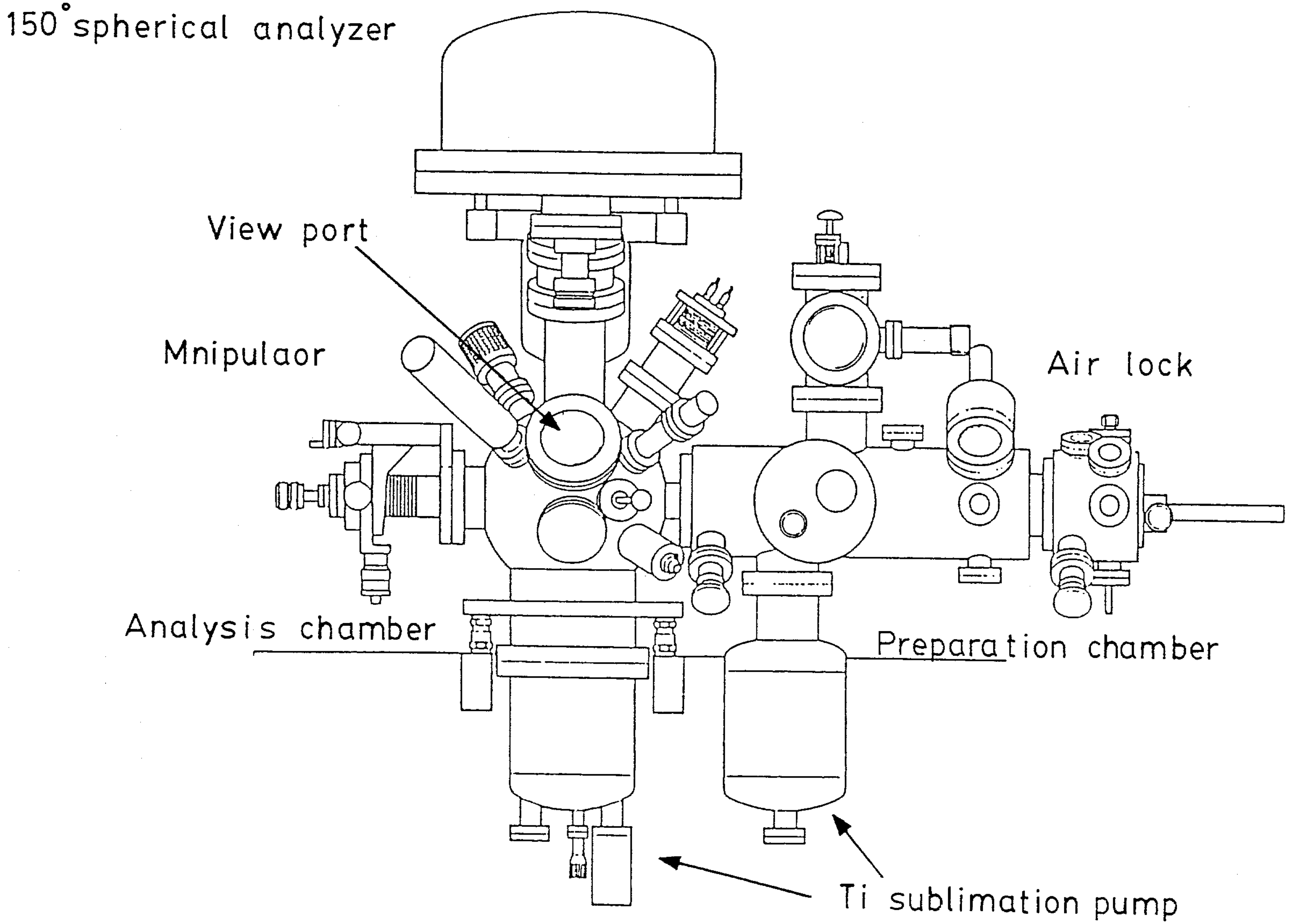


Figure 3. The UHV system on the chamber B.

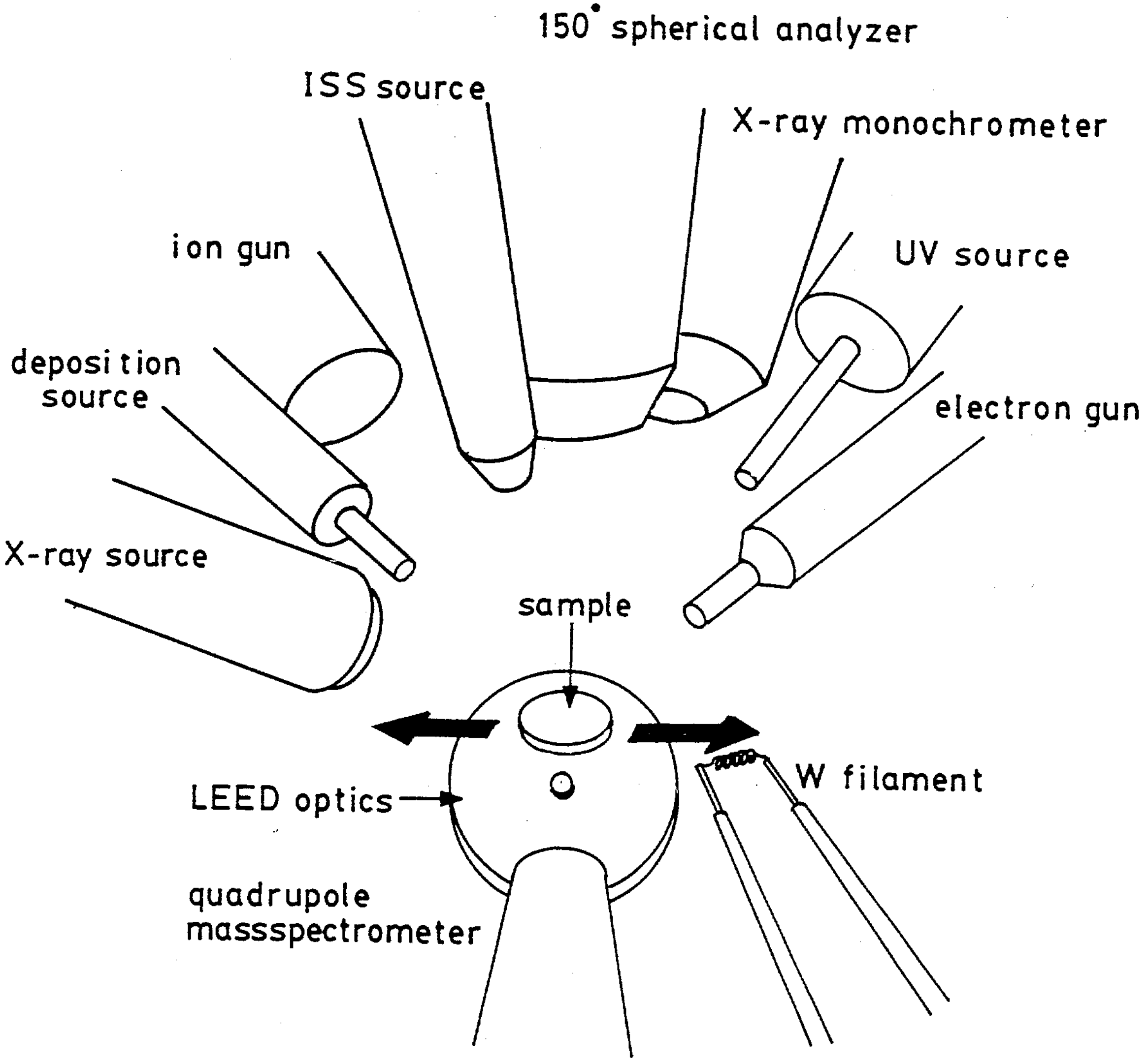


Figure 4. The UHV apparatus in the chamber B.

bombardment, a tungsten filament to produce hydrogen atom, two gas introduction systems and an Al deposition source. This chamber for analysis is equipped with an ion gun for ion scattering spectroscopy (ISS), an electron gun for AES, a dual-anode X-ray source and a ultra violet source for photoelectron spectroscopy to add to a quadrupole mass spectrometer (m/e = 1 ~ 200). The dual-anode X-ray source discharges Al Kα line (hν = 1486.6 eV) and Mg Kα line (hν = 1253.6 eV) independently. The ultra violet source discharges He(I) light (hν = 21.2 eV) by the electric discharge of He. The strongest point in this chamber lies in a three-channeltrons 150° spherical sector analyzer. Spherical sector analyzer is the most "bright" analyzer among the various types of analyzer because the concentration zone of electron is wide. A electron detector composed of three secondary electron magnitudes (channel tron) which can thrice integrate spectrum for one scanning can realize rapid and high S/N measurement.

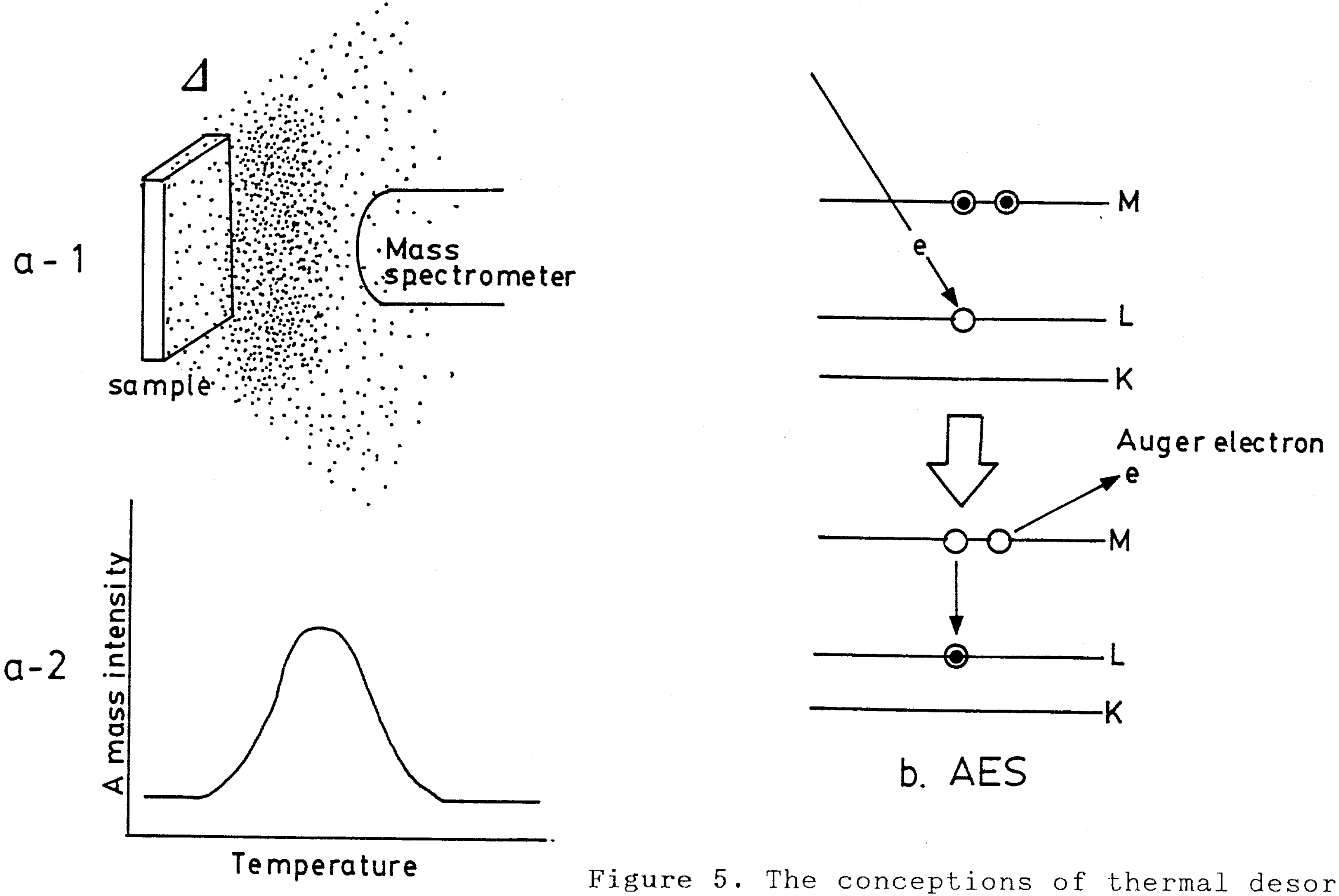
Metal samples attached to manipulators are kept at the temperatures from 90 K to 1300 K by liquid nitrogen and ohmically heating in chamber A and B.

2-3. Surface Analytical Techniques.

There are many methods to analyze the phenomena of surface under UHV. These methods are divided into direct and indirect method. Many direct analyses is based on the analysis for discharged electron. The discharged electron from surface has not only the informations of surface but that of bulk. The spectroscopies used in this study as follows (The conceptions of these spectroscopies are displayed in Figure 5 and 6):

Thermal Desorption Spectroscopy (TDS).

TDS is a representative indirect surface analysis and offers the information of desorbed species. Generally, TDS under UHV is performed by detecting continuously a mass number of a desorbed species by a mass spectrometer where a surface is heated at a constant heating rate (Figure 5a-1). As a result, a TD spectrum shows the change for a mass fragment of a desorbed species as a function of the surface temperature (Figure 5a-2) and offers the temperature of desorption, the assignment and the relative amount of desorbed species. Because desorption obeys rules due to kinetics, the analysis of the line shapes of TD spectra is available for understanding the desorption mechanism in some degree. Although TDS is liable to be slighted because of indirect method, I think TDS to be the simplest and important method among surface analytical techniques.



a. TDS

Figure 5. The conceptions of thermal desorption spectroscopy (TDS) and Auger electron spectroscopy (AES).

Auger electron spectroscopy (AES).

AES is a spectroscopy to analyze the Auger electron discharged from surface by the incident electron of a few keV (Figure 5b) and can sensitively detect elements on surface. For this reason, AES is available for the check of the clean surface and the estimation for the amount of adsorbed species on simple system such as the deposition on surface. AES transition of valence band (for example, Al LMM transition) is very sensitive to reaction. An AES spectrum is measured by either differential mode (dN(E)/dE) or integral mode (N(E)). Although differential mode is frequently used in general, integral mode is superior to differential mode for the interpretation of electronic structure or the fixed quantity.

Photoelectron spectroscopy.

Ultraviolet photoelectron spectroscopy (UPS).
X-ray photoelectron spectroscopy (XPS).

Photoelectron spectroscopy is a spectroscopy to analyze photoelectron from inner and outer shells which is discharged by incident ultraviolet light (Figure 6). Therefore the photoelectron spectrum reflects valence and inner orbitals. In principle, the binding energy of an orbital below the Fermi level (E_B), the kinetic energy for photoelectron (E_K) and work function (ϕ) is simply expressed as follows:

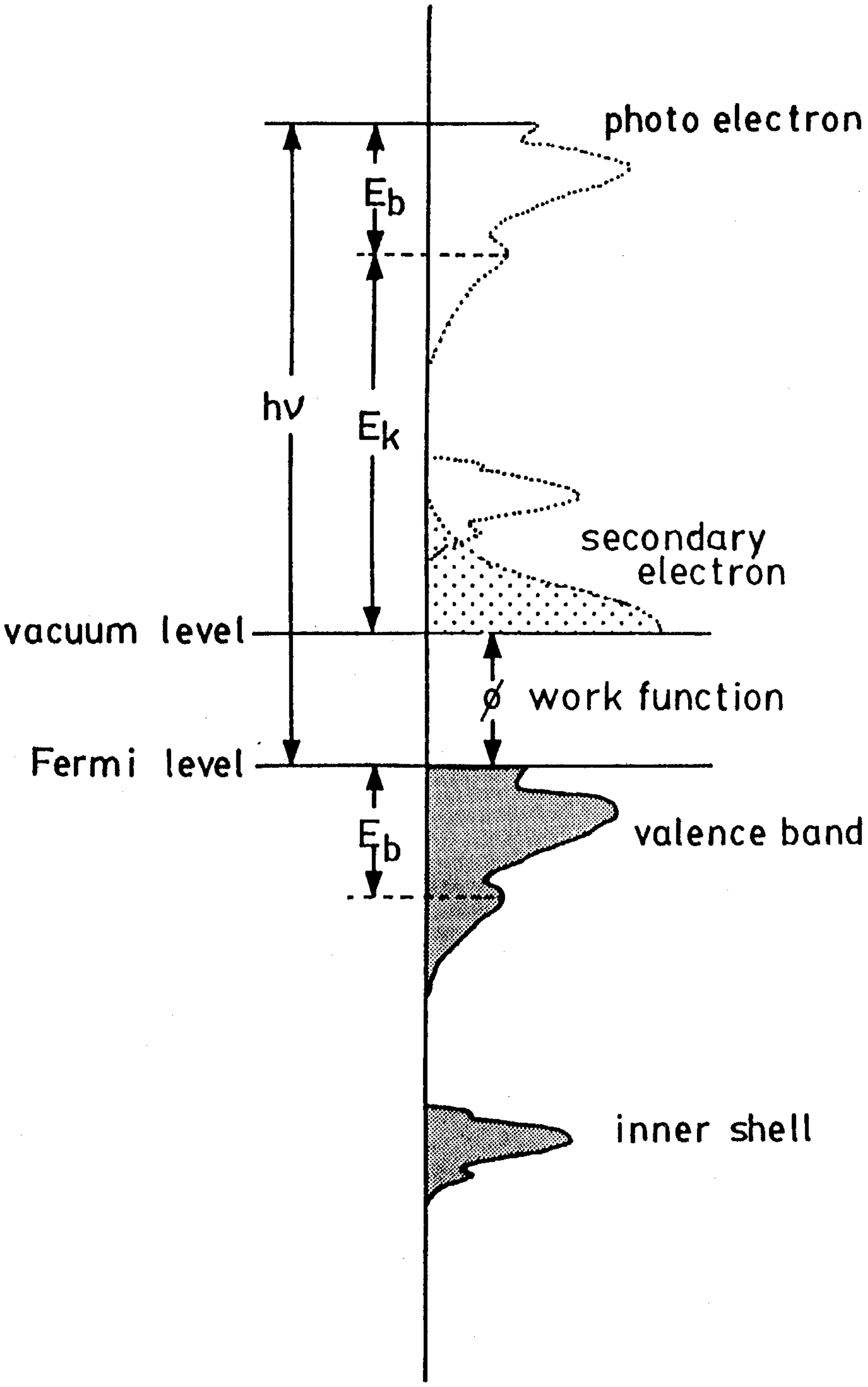


Figure 6. The conception of photoelectron spectroscopy.

$$E_B = h\nu - E_K + \phi$$

where $h\nu$ is the energy of ultraviolet light. Although XPS and UPS are essentially same spectroscopy, XPS conforms to the analysis of inner shells. The eigen line widths of Al $K\alpha$ and Mg $K\alpha$ line for XPS are 680 meV and 830 meV, respectively. Because of these wide line widths, the resolution of XPS is defined by the eigen line widths of exciting lights. On the other hand, the resolution of UPS is 20 meV ~ 40 meV and very high. The Analyzer characteristic determine the resolution of UPS because the He(I) light for UPS has the narrow eigen line width of a 3 meV. Consequently, UPS is available for the detail observation for valence orbitals. In addition, UPS can measure the absolute value of work function ϕ .

Low energy electron diffraction (LEED).

LEED shows the reciprocal lattice image of surface by the diffraction of low energy electron and can observe ordered surface structure. LEED displays its availability to ordered adsorbate on ordered surface but can not offer the informations of disordered adsorbate or adsorbed hydrogen adatom which is hard to diffract electron.

2-4. The preparation and cleaning for Al(111) surface.

By means of a discharge erosion, a rectangular shaped Al(111) single crystal (7 x 7 x 1.2 mm) was cut within 0.5° of the (111) orientation from a single crystal rod of 99.99 % purity whose direction was determined by the Laue back diffraction method method. Figure 7 shows a feature of Al(111) single crystal sample. Two slots (0.2 mm width x 0.5 mm depth) were cut out in upper and lower sides of the crystal edges for mounting the crystal. A hole of 0.4 mm diameter and 1 mm depth as a thermocouple well was bored into the crystal edge by means of the discharge erosion method. The Al(111) single crystal sample was polished by emery papers in order of No.600, 800, 1000, 1200 and 1500 emery paper. Because the sample surface was not as a mirror but muddy after polishing, this surface did not promise plane and smooth Al(111) surface. After the mechanical polishing, a mirror surface was obtained by electropolishing the Al surface (5 A/dm^2, 40 V) in a solution of water 1, $HClO_2$ (d = 1.6) 37 and CH_3COOH 153 dm^3. Two tantalum wires of 0.3 mm diameter were fastened through the precut slots of the sample were attached to a sample holder. The crystal was heated effectively by thermal conduction from the ohmically heated tantalum wires. A chromel-alumel thermocouple (0.4 mm diameter) was insert into the pre-bored thermocouple well.

To clean the Al(111) surface, the operation of Ar^+ bombardment (Ar 5 x 10^{-5} torr, 500 V) at room temperature

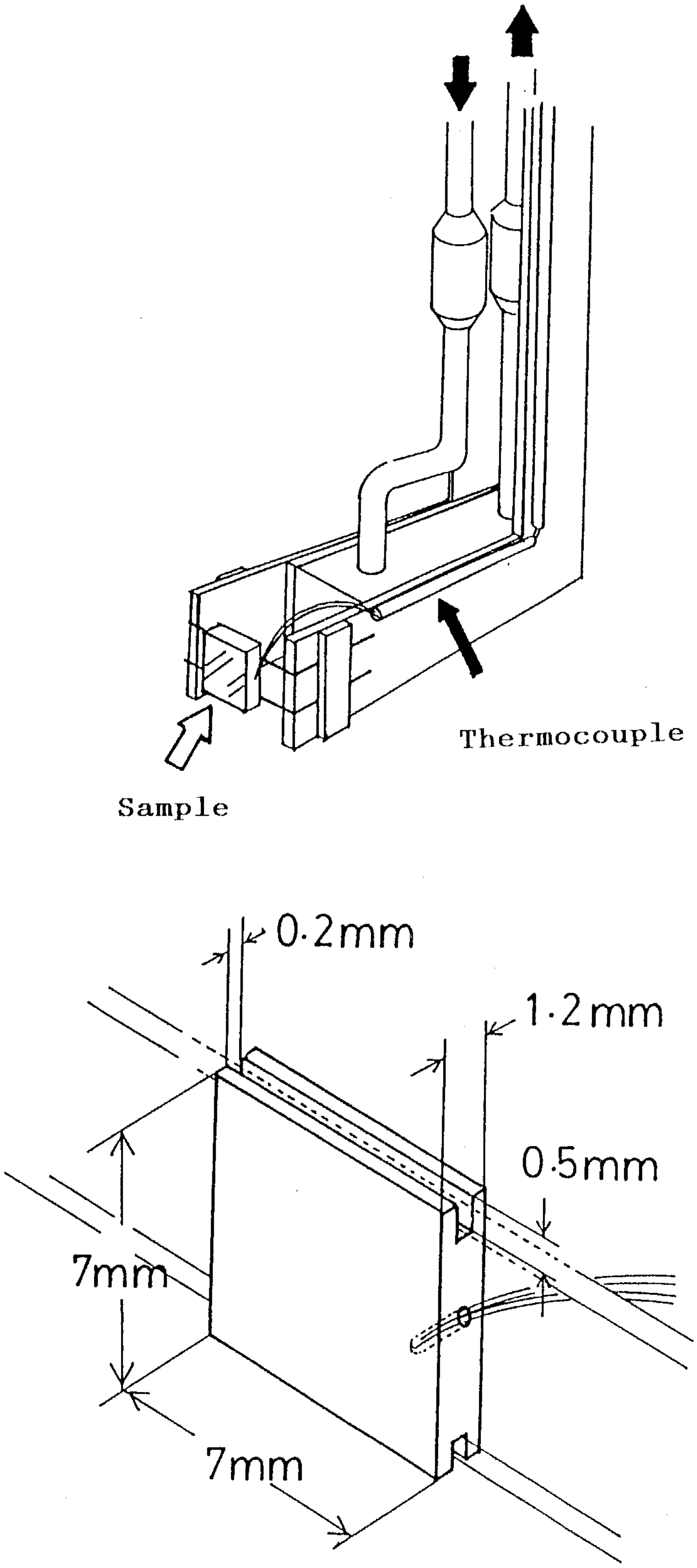


Figure 7. An Al(111) single crystal sample (A) and the attachment of the sample to a manipulator.

for 1 hour and annealing for 1 hour at 723 K was repeatedly performed. AES measurements revealed that even the Ar^+ bombardment of 48 hour in total could not almost reduce oxygen and carbon on the surface and an thick alumina layer existed near surface. This suggested that the polish method was wrong. Electropolishing smoothes uneven surface, but on the other hand it forms strong and thick oxide layer more than a few μ m near surface.[1] The mirror-looking surface which is made by electropolishing is due to the thick oxide layer. Therefore the electropolishing for the Al surface is considered to be unsuitable to obtain atomically clean Al surface because Ar^+ bombardment can not remove all of hard and thick alumina layer.

Therefore we prepared the smooth surface by only mechanical polish method. After the polishing of No.1500 emery paper, the crystal was polished by a 1 μ m and a subsequent 0.25 μ m diamond paste on a polishing cloth (BUEHLER LTD.) attached to a smooth mirror. AES spectrum for the mirror Al surface obtained by these process is shown in Figure 8A. The AES spectra in Figure 8 were measured by differential mode (dN(E)/dE). One can recognize Al LVV transition due to alumina, C KLL and O KLL transition to appear at around 50 eV, 270 eV and 500 eV, respectively. Figure 8B displays the AES spectrum of the Al surface after the Ar^+ bombardment of 5 hour in total (5 cycles of Ar^+ bombardment for 1 hour and subsequent annealing at 723 K for 1 hour). The signals of C and O are less than the sensibility of AES although only Al

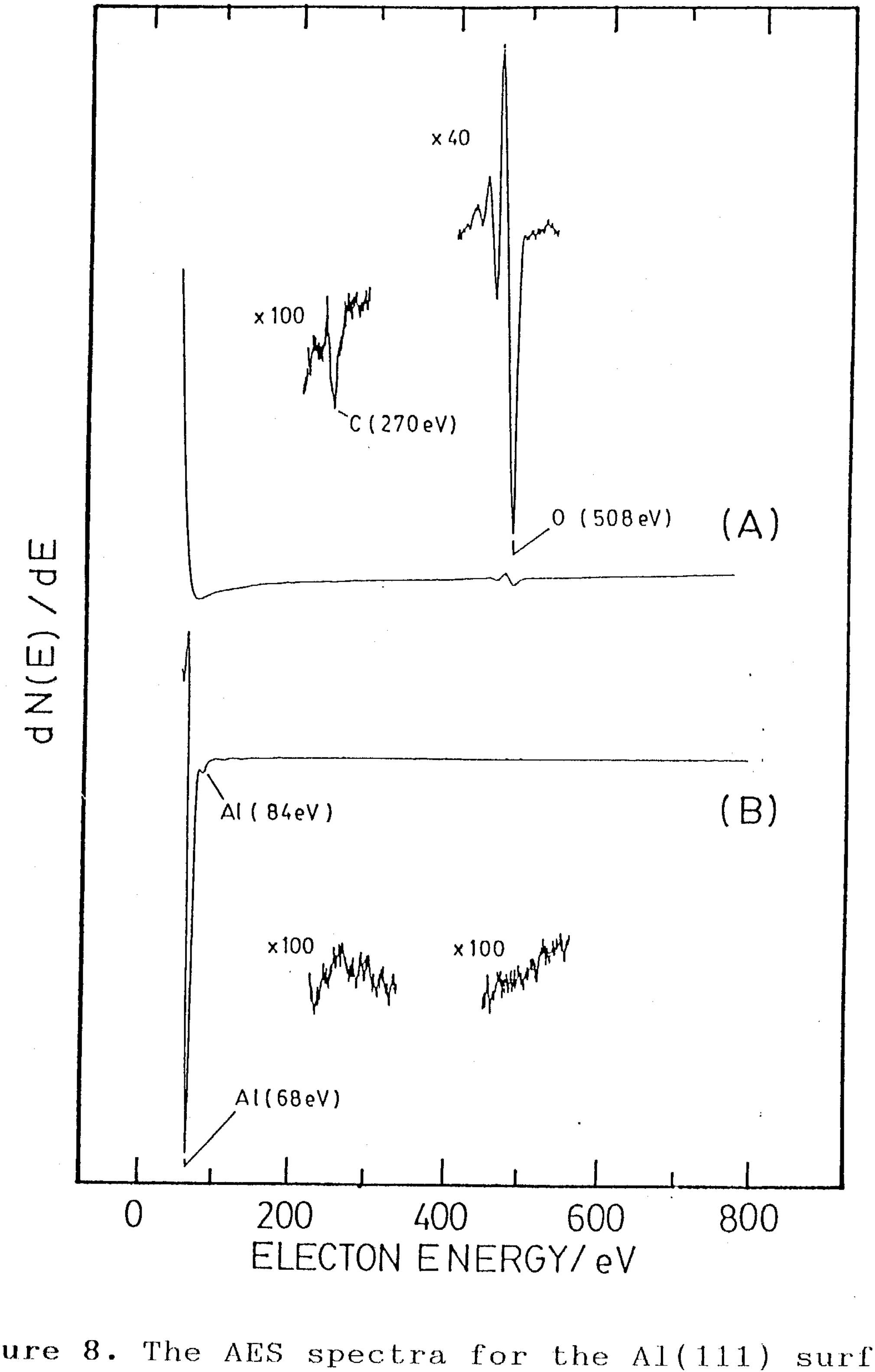


Figure 8. The AES spectra for the Al(111) surface. A. Before cleaning. B. After cleaning.

LMM transition due to metallic Al is shown at 68 eV in spectrum B. LEED showed the sharp hexagonal LEED spots attributed to the (111) surface of f.c.c. crystal. These results means that this preparation and cleaning process for the Al surface lead to an atomically clean Al(111) surface. Increasing the acceleration energy of Ar^+ from 500 V to 3 KV, the atomically clean Al(111) surface was obtained within 2 hour.

Generally, to obtain the atomically clean Al(111) surface, the cycle of Ar^+ bombardment and annealing have to be repeated more than a whole day and night.[2] However the Al(111) single crystal prepared by the method mentioned above can rapidly become the atomically clean surface.

2-5. References.

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3. Surface reaction of CH_2I_2 with an Al(111) surface.

1. Introduction.

The chemistry of organometallic compounds has developed remarkably since 1950's and played an important role in industry.[1] Organometallic compounds of non-transition metals have its characteristic features.[1] The alkyl ligands of organometallic compounds on non-transition metals such as Mg, Zn and Al show strong reactivity as carbanions. An example of this characteristic reactivity is alkylation reactions. Furthermore, it is well known that non-transiton metals react directly with alkylhalides (RX) and form alkylaluminumseskihalides like $R_3Al_2X_3$, RMgX and RZnX, respectively. The reaction between Mg and RX leads to the formation of the Grignard Reagent and has been widely used for the synthesis of a variety of alcohols. These organometallic compounds of non-transition metals are formed by reactions between corresponding solid metal surfaces and hydrocarbonhalides, however, little has been known about these surface reactions.

Up to now, reactions of non-transition metal surfaces with alkylhalides have been investigated by means of surface analytical techniques under ultrahigh vacuum (UHV). A study of CH_3Br/Mg(0001) surface reaction was carried out using high resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS) and thermal desorption (TD).[2] This study reported that adsorbed CH_3Br was already decomposed at 123 K and was lead to facile production of surface bromide (Mg-Br) accompanied with formation of gaseous ethane. Yates and his coworkers investigated reactions between methylhalides and an Al(111) surface.[3] They reported that CH_3I was decomposed on the surface at 150 K and a methylidyne group ($\equiv$ C-H) and an Al-I bond were identified on the surface by means of HREELS. Although these attemption revealed the reactivity between hydrocarbon halides and non-transition metal surfaces to be very high, the formation of organometallic compounds could not be confirmed.

Recently, we found out that CH_2I_2 reacts with an Al(111) surface below 200 K where ethylene desorb from the surface.[4,5] These reactions have a close similarity to the Simmons-Smith reaction.[5] The Simmons-Smith reaction generates a carbene (:CH_2) through an organozinc compound formed by the reaction between Zn and CH_2I_2.[6] Without alkene the Simmons-Smith reaction proceeds forming ethylene by the coupling of carbenes; other olefins are not formed. When alkene coexsits, on the other hand, cyclopropane derivatives are formed by the insertion of the carbene to a C=C bond of alkene. The mechanism of the carbene formation has been considered as follows;

$$2CH_2I_2 + 2Zn \rightarrow 2[I\text{-}Zn\text{-}CH_2\text{-}I] \rightarrow 2ZnI_2 + 2\text{":}CH_2\text{"}$$
$$\rightarrow 2ZnI_2 + C_2H_4 .$$

The reaction of CH_2I_2 on Al(111), which produces ethylene, resembles the Simmons-Smith reaction. Therefore, it is worth studying details of the reaction of CH_2I_2 on Al(111).

In this study the generation of organoaluminum compounds and ethylene through the reaction between CH_2I_2 and Al(111) has been studied by means of surface analytical techniques under UHV. This study reveals a completely different aspect of the surface chemistry of non-transition metals with that of transition metals :An organometallic compound desorbs by the reaction between an adsorbate and a metal surface.

2. Experimental.

All the experiments were carried out in a stainless steel UHV apparatus (the UHV chamber A shown in Figure 1 of section 2) with typical base pressure lower than 2 x 10^{-10} torr. The Al(111) surface was cleaned by cycles of Ar^+ bombardment at room temperature and annealing at 723 K and cleaness of the surface was confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED).

The clean Al(111) surface was cooled down to 108 K by liquid N_2 before exposure to CH_2I_2 through a doser made by a glass microchannel plate. CH_2I_2 was dosed to the surface held at 108 K unless otherwise stated. After the dosage of CH_2I_2 onto the surface, CH_2I_2/Al(111) was investigated by means of TD, AES and LEED. CH_2I_2 (>99.9 % purity) was purchased from Kanto chemical Co. Ltd. and used after purification by freeze-pump-thaw cycles. CH_2I_2 pressure in the backside of the gas

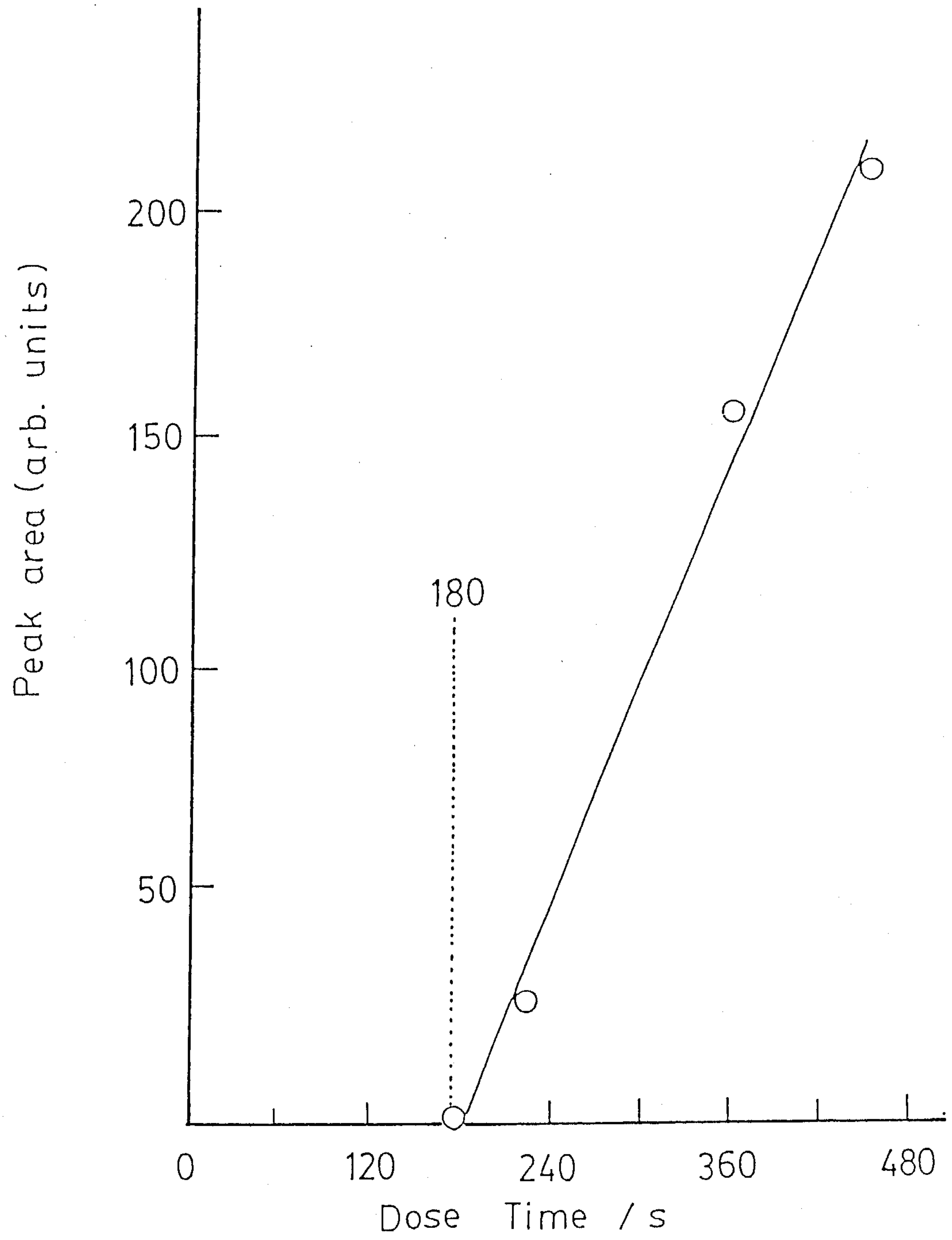

Figure 1. TD peak intensities of $CH_2I_2^+$ (m/e=268) with varying dosage time of CH_2I_2.

doser was kept constant value of 2 x 10^{-3} torr for all experiments. Thus the flux of CH_2I_2 from the gas doser was kept constant. Exposures of CH_2I_2 on the surface were controlled by dosing time. TD experiments were carried out with the heating rate of 15 K/s. Desorbed species were detected by means of a quadrupole mass spectrometer (ANELVA AGA-360). Auger spectra were recorded in a dN(E)/dE mode with a LEED optics at primary beam energy of 1.7 KeV and sample electron current of 5 μA.

3. Results and discussion.

3-1. Reaction of CH_2I_2 with Al(111).

In TD experiments, the completion of one monolayer usually conforms to the appearance of the peak of a physisorbed state with increasing the coverage of reactant.[7] In CH_2I_2/Al(111) a TD peak of $CH_2I_2^+$(m/e=268) appeared at about 190 K. Figure 1 plots TD peak intensity of $CH_2I_2^+$ with varying dosage time. Since CH_2I_2 did not desorb at all below the dosage time of 180 s, we defined the amount of adsorbed CH_2I_2 for the dosage time of 180 s as 1 monolayer (ML).[4]

In the course of experiments, we found out that AES intensities of C and I for the CH_2I_2 adsorbed Al(111) surface changed profoundly depending on the sample annealing temperature. The temperature dependence of AES intensity ratios of C(KLL, 270 eV)/Al(LMM, 68 eV) and I(MNN, 510

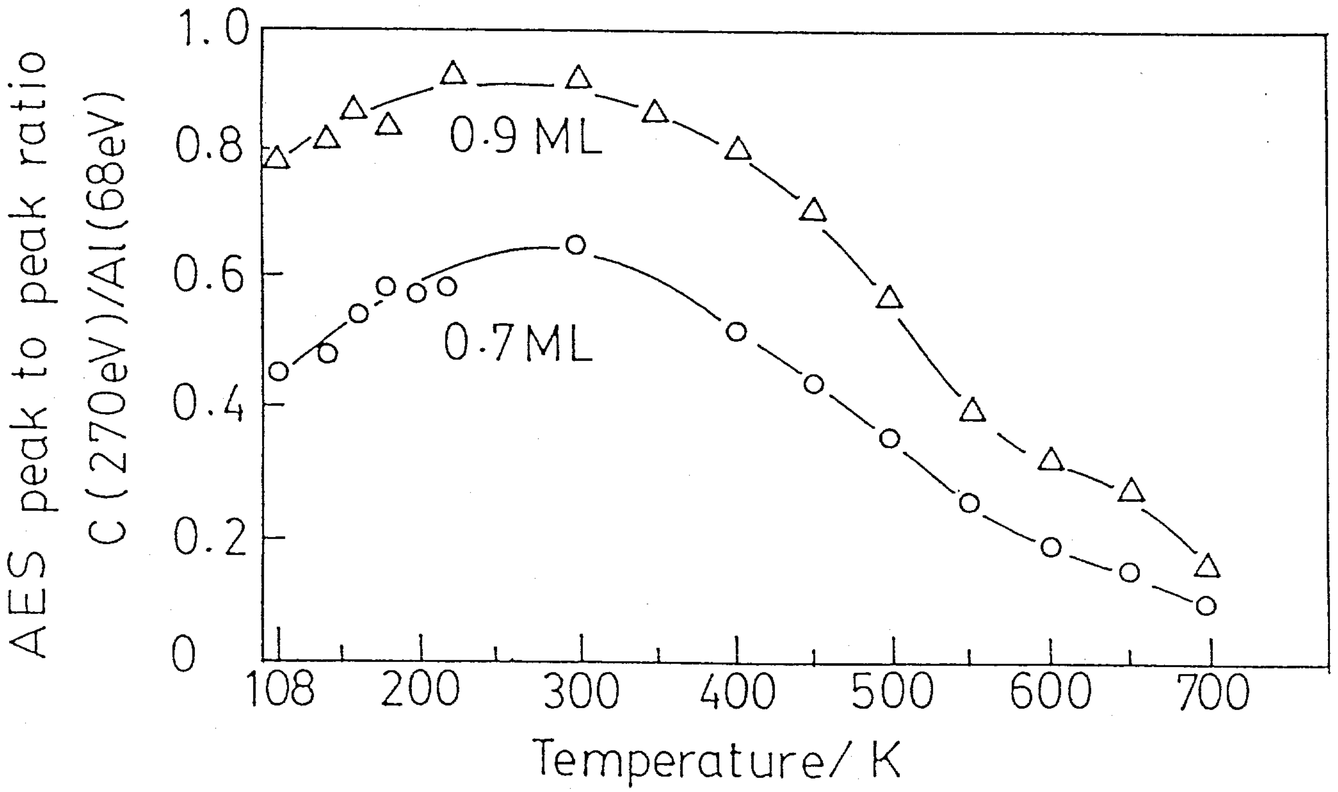

Figure 2. AES peak-to-peak ratios (C(270 eV)/Al(68 eV)) of CH_2I_2/Al(111) as a function of temperatures.

eV)/Al(68 eV) was, thus, measured by varying the adsorbed amount of CH_2I_2 on the surface. Representative results are plotted as a function of sample temperature for the CH_2I_2 coverages of 0.7 ML and 0.9 ML as shown in Figure 2 and 3, respectively. The sample was heated to the indicated temperatures with heating rate of 2 K/s. Immediately after the sample temperature reached the indicated value, the sample was cooled down to 100 K - 120 K for AES measurement. Since TD spectra of all desorbed species (see below) did not change before and after AES measurements, the electron beam induced decomposition and desorption of the adsorbate were not significant. The intensity ratio of C/Al increased with increasing the annealing temperature up to ca. 300 K as shown in Figure 2. The intensity ratios at around room temperature were considerably larger than those at low temperature. No species desorbed below 300 K from the surface precovered by CH_2I_2 to less than 1 ML. Therefore, the temperature dependence of the AES ratios indicates that CH_2I_2 has reacted on the Al(111) surface and a part of carbon species has been located beneath the outermost surface even at 108 K. Generally, the reactivity of hydrocarbon halides with non-transition metals depends mainly on a kind of metals and the carbon-halogen bond strength. For example, when several methyl halides (CH_3Cl, CH_3Br, CH_3I) were adsorbed on an Al(111) clean surface, only CH_3I reacted with the surface and decomposed at 150 K.[3] As for the other combination of methyl halides and non-transition metals, Dubois, et. al. reported that the decomposition of

CH_3Br was already observed at 123 K on a Mg(0001) surface.[2] Thus the reaction between hydrocarbon halides and non-transition metals occurs and the carbon-halogen bond of hydrocarbon halides decomposes on the surface. Therefore, it is not unexpected that CH_2I_2 reacts with the Al(111) at 108 K. From these results, this reaction may be regarded as a kind of corrosion. Corrosion without water i.e. dry corrosion, occurs on metal surfaces with oxidant gases such as halogen and sulfur at relatively high temperature.[8,9] To our best knowledge, dry corrosion has not been reported at such low temperature as 108 K.

In opposition to the behavior of carbon species, the AES peak intensity ratios of I/Al were almost constant below 400 K as shown in Figure 3. This behavior of carbon and iodine species is expected to have some relation to the formation of an alkyl-aluminum bond on the surface as described in the subsequent section. Although LEED spots became obscured after adsorption of 1 ML CH_2I_2, it could be still observed below 350 K. Therefore, this reaction proceeds keeping the surface and subsurface structure of Al(111) to a certain degree. Above 300 K the C/Al ratio decreased in intensity with increasing the annealing temperature as shown in Figure 2. A part of carbon still remains on the surface at 700 K as carbide.[3] To remove this carbidic carbon lengthy cleaning cycles were necessary before each experiment. The I/Al ratio decreased in intensity also above 400 K and surface iodide completely vanished from the surface at 700 K as shown in Figure 3. The

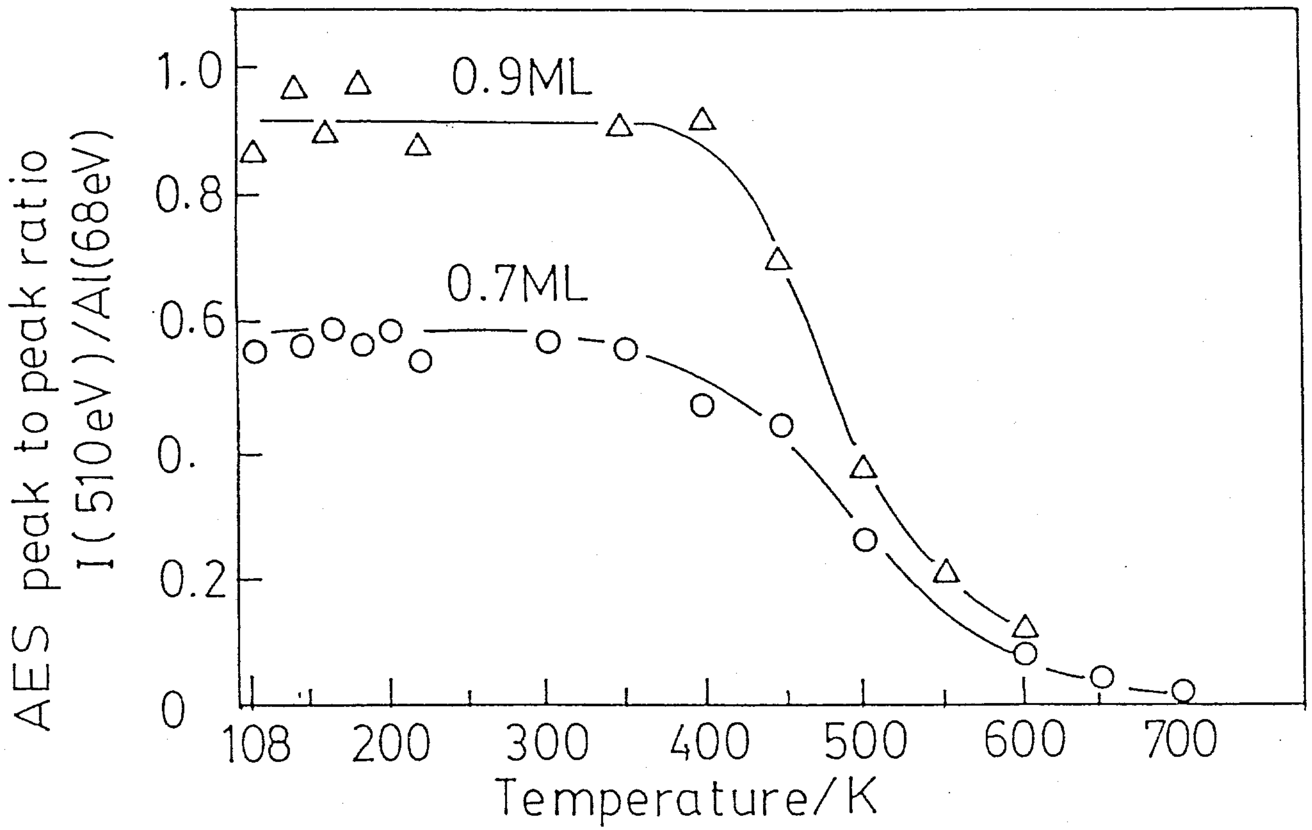

Figure 3. AES peak-to-peak ratios (I(510 eV)/Al(68 eV)) of CH_2I_2/Al(111) as a function of temperatures.

decrease of carbon and iodine above 400 K suggests the desorption of compounds which contain these atoms. The results are consistent with TD experiments described below.

3-2 Assignment of desorbed species from CH_2I_2/Al(111).

To obtain further information about the reaction between CH_2I_2 and the Al(111) surface, TD spectra of various mass numbers were measured with varying CH_2I_2 coverage. Before discussing the reaction on the surface in detail, we will assign desorbed species observed by TD experiments. Although TD spectra were rather complicated, the formulas of almost all the desorbed species were determined by carefully comparing the TD spectra for various fragments .

It turned out that TD spectra of m/e=27 give representative results for desorbed species. We will, thus, explain characteristic features of desorbed species by using TD spectra of m/e=27. Figure 4 shows TD spectra of m/e=27 from CH_2I_2/Al(111). No desorbed species was observed below 300 K from the surface precovered by CH_2I_2 to less than 1 ML. A TD peak of m/e=27 appeared at ca. 140 K for 1 ML CH_2I_2. This peak shifted to 150 K and increased in intensity with CH_2I_2 coverage. A TD peak of m/e=28 was also observed at 140 K-150 K above 1 ML. The cracking ratio of m/e=28 and 27 for ethylene was about 100/70 with the mass spectrometer used in the

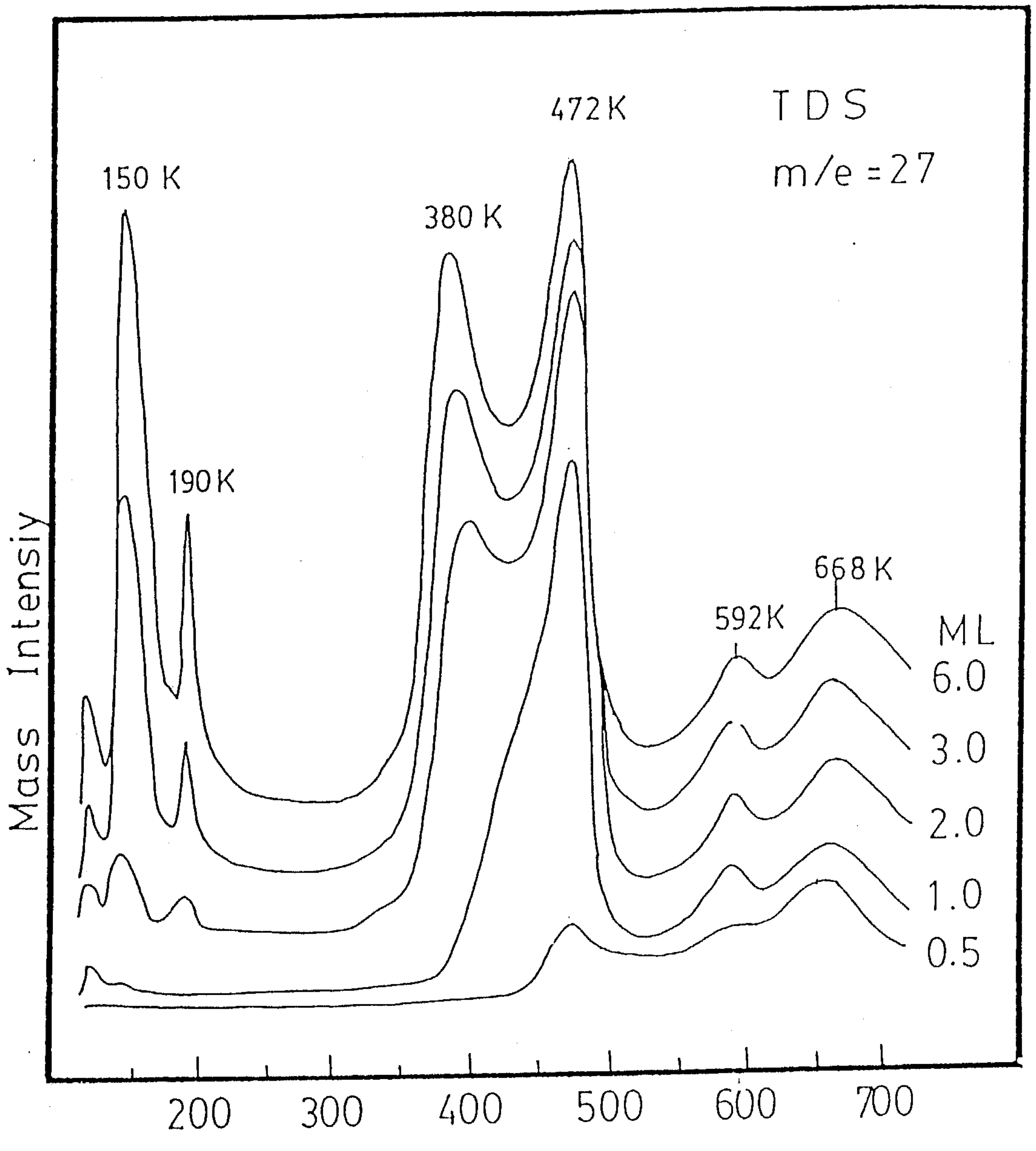

Figure 4. TD spectra of m/e=27 for CH_2I_2/Al(111) at various CH_2I_2 coverage.

experiments. Since the TD peak intensity ratio of m/e=28 ($C_2H_4^+$) and m/e=27 ($C_2H_3^+$) was 100/70 at the same coverage,[4,5] these TD peaks were attributed to the desorption of ethylene (C_2H_4).[4,5] Therefore, it was made clear that ethylene begins to desorb at around 150 K above 1 ML as shown in Figure 4. We will discuss the mechanism of the formation of ethylene in the subsequent section.

A TD peak of m/e=27 also appeared at 190 K. The peak temperature did not shift so much with CH_2I_2 coverage. Parent molecules (CH_2I_2) desorbed also at 190 K. The peak was assigned to spurious cracking products of desorbed CH_2I_2 in the mass spectrometer because the coverage dependence of the position and shape for the TD peak of m/e=27 coincided with those of CH_2I_2 ($CH_2I_2^+$, m/e=268). This assignment was ascertained because we detected the m/e=27 mass signal on introducing CH_2I_2 into the chamber.[4]

There were four TD peaks of m/e=27 above 300 K; these peaks appeared at around 380 K, 472 K, 592 K and 668 K as shown in Figure 4. Since no TD signals for m/e=28 and 26 were observed above 300 K under the same experimental condition as that for Figure 4,[4] these four TD peaks above 300 K were not due to the desorption of ethylene or other hydrocarbons. Thus these peaks were assigned to Al^+ (m/e=27) produced by the fragmentation of desorbed aluminum compounds from the surface.[4]

To determine the formulas of these four aluminum compounds desorbed from the Al(111) surface above 300 K, TD spectra of various mass numbers were measured at the coverage of 1 ML CH_2I_2. Figure 5 shows TD spectra of m/e=2, 27, 154, 155, 169, 170 and m/e>200. TD spectrum of m/e>200 was measured by means of the high pass filter mode of the mass spectrometer; the summation of all species from m/e= 200 to ca. 700 was measured by this mode. No TD signals were detected for m/e=156-168 and 171-200 under the same experimental condition. By taking into account the above results the formulas of four aluminum compounds desorbed above 300 K were determined as follows:

Firstly, we assigned the TD peak at 380 K in Figure 4. This peak appeared at 416 K and 1 ML as a shoulder of the peak at 472 K and grew into the peak at 380 K with CH_2I_2 exposure as shown in Figure 4. TD spectra of m/e=27 and 154 had also shoulders at 416 K as shown in Figure 5. Moreover, no peaks for TD spectra of any hydrocarbon fragments were observed at 416 K. Accordingly, the mass number of 154 could be assigned to AlI^+. The aluminum compound desorbed at 416 K was, therefore, composed of only Al and I atoms. We determined that these peaks are due to the desorption of aluminum iodide (AlI_3) because the shoulder was also observed at 416 K for a TD spectrum of m/e>200 as shown in Figure 5,.

Secondly, we assigned the TD peak at 472 K in Figure 4. The peak did not shift so much with CH_2I_2 exposure. At 1 ML CH_2I_2 coverage TD spectra gave the peaks at 472 K for m/e=2, 27, 154, 155, 169, 170 and >200 as shown in Figure 5. Since no desorption peak was observed at 472 K for m/e=171-200, the

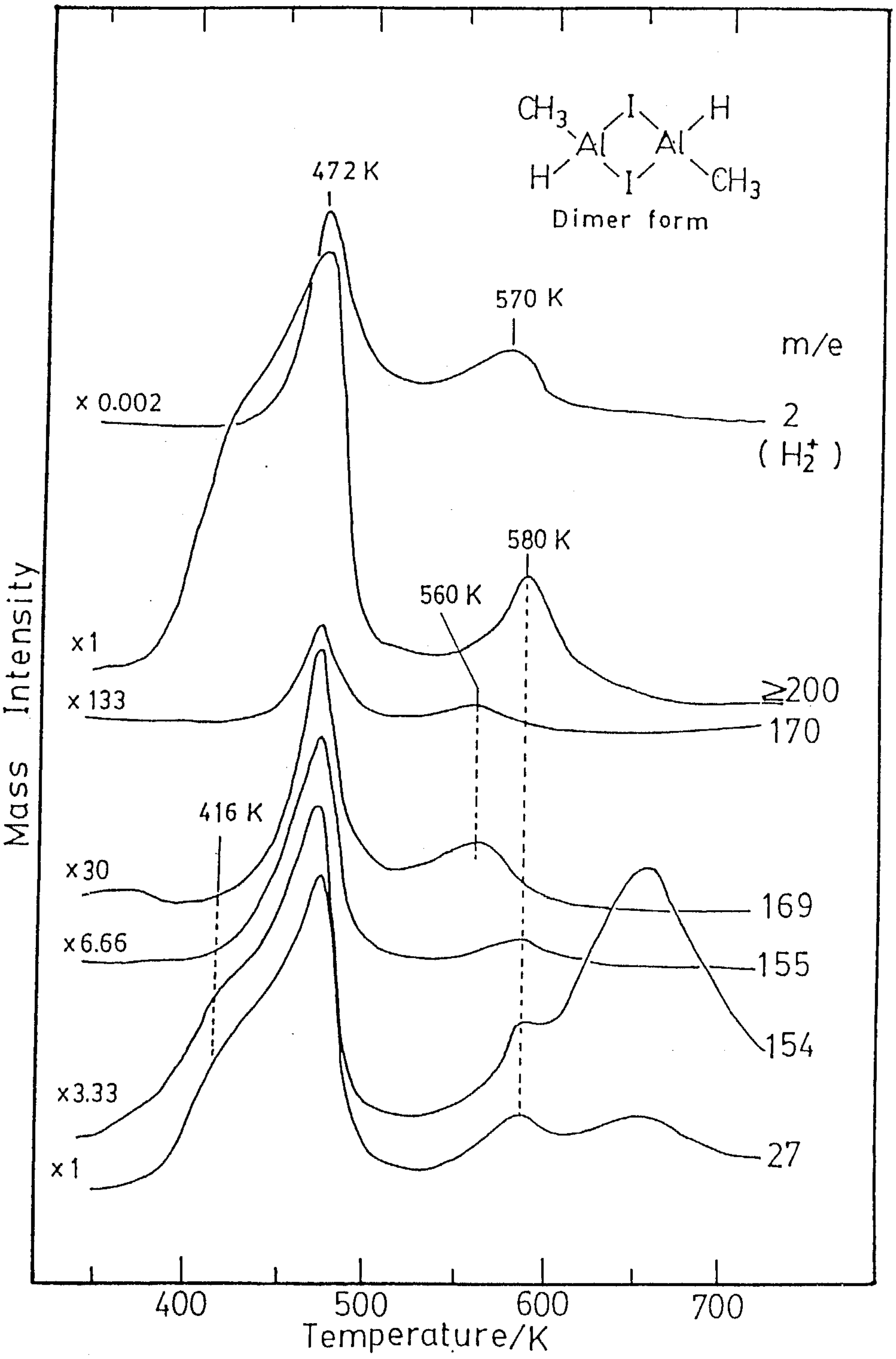

Figure 5. TD spectra of various mass number for 1 ML CH_2I_2/Al(111).

peaks of mass numbers of 154 and 155 could be assigned as AlI^+ and $HAlI^+$, respectively. TD peaks of m/e=169 and 170 at 472 K were attributed to CH_3AlI^+ and $CH_3Al(H)I^+$ (hydroiodomethylaluminum), respectively.[4] Although these were all the fragments of the organoaluminum compound detected below the mass number of 200, TD signal of m/e>200 was also detected at this temperature as shown in Figure 5. Thus the possible candidate of the desorbed organoaluminum compound should have the mass number of more than m/e=200 and can afford CH_3AlI^+ and $(CH_3Al(H)I)^+$ as fragments. Aluminum compounds such as alkylaluminum halides are liable to form dimers with the three center bond consisting of two Al atoms and a halogen atom.[10] By taking into account both the possible combination of fragments detected and the tendency of facile formation of a dimerized compound, it is highly probable that the dimer of $CH_3Al(H)I$ desorbs from the surface; the model of the dimer is shown in an inset of Figure 5.[4] To our knowledge, this is the first direct observation of an organometallic compound produced by a reaction between an adsorbate and a solid surface. We represent the desorbed organoaluminum compound as $CH_3Al(H)I$ in this paper.

Thirdly, we assigned the TD peak at 592 K in Figure 4. The TD peak appeared at about 580 K below 1 ML and shifted to 592 K with CH_2I_2 exposure. As can be seen in Figure 5, TD peak of Al^+(m/e=27), AlI^+ (m/e=154) and $HAlI^+$ (m/e=155) appeared simultaneously at this temperature. TD signal between m/e=156 and 200 was not detected. Although TD signal of m/e>200 was detected, no desorbed species containing carbon atoms was observed above 560 K in the TD experiments. These results indicate that a compound exclusively composed of Al, H and I desorbs at about 580 K. It is interesting to note that the TD peak of H_2^+ was not observed at this temperature. This result indicates that the desorbed compound has only one hydrogen atom. We concluded that $AlHI_2$ or its dimerized form are the most probable candidates for the aluminum compound desorbed at 580 K. We represent the desorbed hydroiodoaluminum compound as $Al(H)I_2$ in this paper.

Lastly, we assigned the TD peak at 668 K in Figure 4. This peak appeared at about 650 K below 1 ML and shifted to 668 K with CH_2I_2 coverage. A TD peak for AlI^+ (m/e=154) appeared at 655 K as is shown in Figure 5,. Since no TD signals of the other mass numbers except m/e=27 (Al^+) and 154 (AlI^+) were observed at 655 K, we concluded that AlI itself desorbs at this temperature. AlI is known as aluminum iodide with an aluminum of the low valence state.[11] The thermal decomposition of a surface compound, which is composed of aluminum and iodine, might lead to the desorption of AlI at 646 K.

In Figure 5 there is a peak for m/e=2 at 570 K. Since there was no corresponding peak of other mass number at this temperature as shown in Figure 5, this peak was assingend to the desorption of H_2. Although the desorption of H_2 at this temperature is surely conjugated with the some surface reaction, the detailed mechanism of the desorption is not clear.

TD peaks of m/e=169 and 170 were detected at 560 K as shown in Figure 5. The desorbed species at this temperature is not an aluminum compound because TD signal of Al^+ was not observed at 560 K. Thus the peaks of m/e=169 and 170 at 560 K are probably attributed to the desorption of iodopropane (C_3H_7I).[4]

As a result of the above discussion, almost all desorbed species were assigned. The assignment of aluminum compounds desorbed from CH_2I_2/Al(111) are summarized in Table 1.

3-3 Formation and desorption of organoaluminum compounds.

It is interesting to note that TD peaks of H_2^+ and $CH_3Al(H)I^+$ at 472 K showed similar peak shapes and behavior with CH_2I_2 coverage. The intensity ratio of the TD peak areas for H^+ and H_2^+ at around 472 K was 20/1000 and was almost equal to the fragmentation ratio (H^+/H_2^+) of H_2 (> 99.99999 % purity) measured in the mass spectrometer; the fragmentation ratio was 13/1000. As a result, the most part of the TD signal of H_2^+ at 472 K is not due to the fragmentation of $CH_3Al(H)I$ but to H_2 desorbed independently from the surface. Figure 6 displays the dependence of the intensities of TD peaks for H_2^+ (m/e=2) and CH_3AlI^+ (m/e=169) due to desorbed $CH_3Al(H)I$ at 472 K with the coverage of CH_2I_2 at 108 K. Although the plot of H_2^+ is similar to that of CH_3AlI^+ for a wide coverage range as

Table 1 Desorbed aluminum compound from CH_2I_2/Al(111)

Temperature of desorption	Detected mass number	Desorbed species
380 K——416 K	27(Al^+), 154(AlI^+), >200	AlI_3
472 K	27, 154, 155($HAlI^+$), 169(CH_3AlI^+), 170($CH_3Al(H)I^+$), >200	$CH_3Al(H)I$
580 K——592 K	27, 154, 155, >200	$AlHI_2$
650 K——668 K	27, 154	AlI

shown in Figure 6, these are not identical. Especially the TD peak intensity of CH_3AlI^+ is not proportional to the coverage of CH_2I_2 below 1 ML. On the contrary, the TD peak intensity of H_2^+ is proportional to the coverage below 1ML. This again supports that H_2 desorbs from the surface as a separate molecule at 472 K. These facts strongly suggest that H_2 and $CH_3Al(H)I$ come from a common surface compound. The desorption of H_2 at 472 K is likely to occur through the decomposition of the Al-H bond of the surface compound. Generally, H_2 desorbs from hydrogen adsorbed metal surfaces around 300 K. The temperature of hydrogen desorption (472 K) from the Al-H bond on the CH_2I_2 adsorbed Al(111) surface is somewhat higher than that of general occasion. This is indicative of more stabilized Al-H bond in this surface precursor. A solid aluminum hydride (AlH_3), whose ΔG (298 K) is + 46.6 $kJmol^{-1}$, is unstable and is decomposed into H_2 and Al above room temperature.[12] On the other hand, the Al-H bond in the desorbed $CH_3Al(H)I$ is stable even at 472 K which is the desorption temperature. As a result, the Al-H bond which is stable in the surface precursor is likely to become unstable when $CH_3Al(H)I$ desorbs from the precursor. The decomposition of this unstable Al-H bond might cause the simultaneous desorption of $CH_3Al(H)I$ and H_2.

Hydroiodomethylaluminum ($CH_3Al(H)I$) involves an Al-H bond and a CH_3-Al bond. It is expected that the Al-H bond and the CH_3-Al bond are involved in the surface compound or formed as a result of decompositions of the precursor compound. The

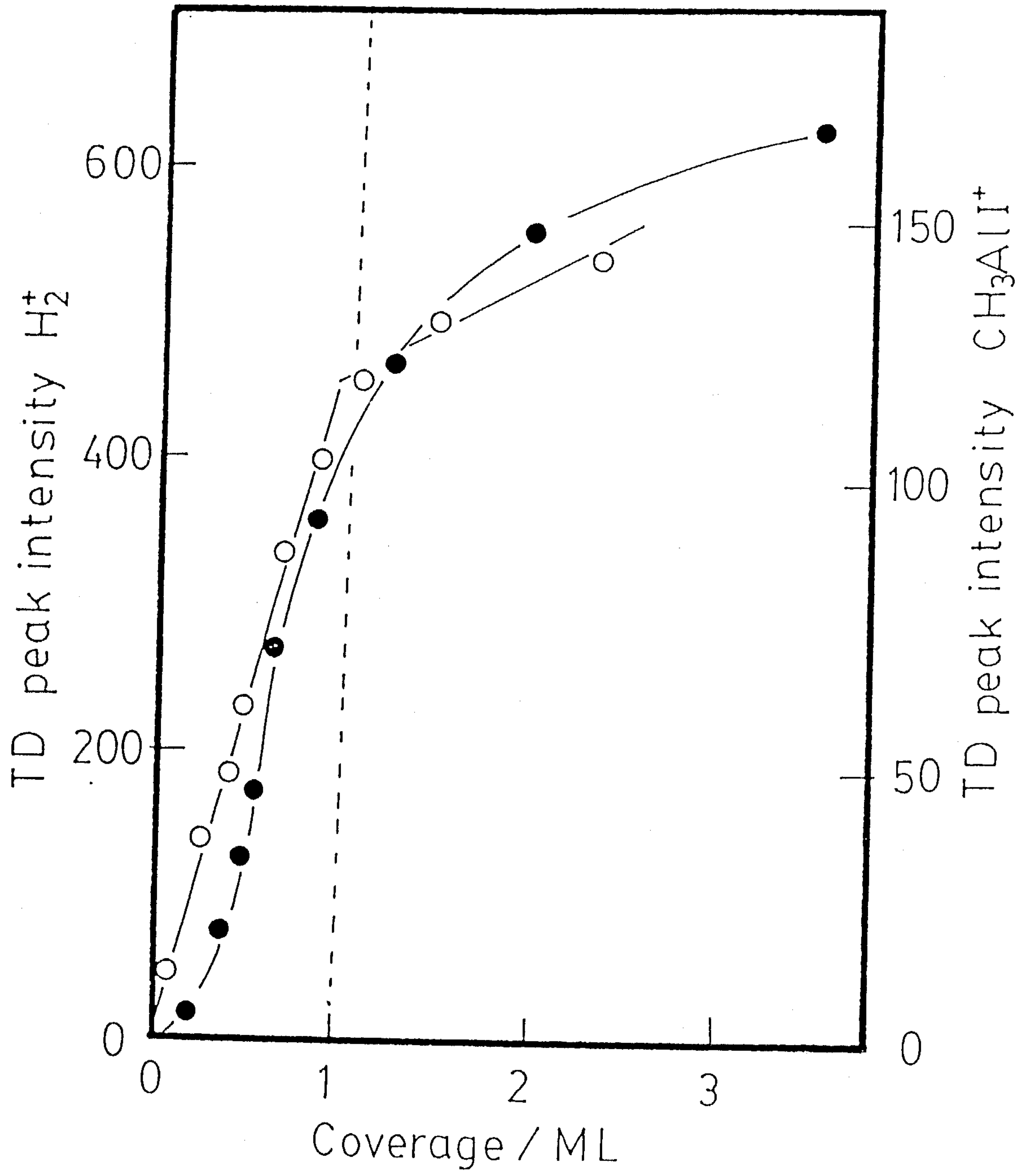

Figure 6. TD peak areas of H_2^+ (m/e=2) and CH_3AlI^+ (m/e=169) as a function of CH_2I_2 coverages. open circle : H_2^+, closed circle : CH_3AlI^+.

simultaneous desorption of $CH_3Al(H)I$ and H_2 mentioned above also supports this. In the chemistry of organometallic compounds, it is known that an alkyl-Al bond is formed through the reaction between an Al-H bond of an organoaluminum compound and a C=C bond of alkene.[1] The Simmons-Smith reaction shows that the CH_2 moiety of CH_2I_2 behaves as carbene ($:CH_2$).[6] Accordingly the CH_3-Al bond may be formed by the insertion of the CH_2 group into the Al-H bond. Considering these facts, it is expected that two CH_2I_2 molecules must be involved at least to form the precursor compound which leads to a $CH_3Al(H)I$ molecule. One CH_2I_2 is consumed to form an Al-H bond, while the other CH_2I_2 produces a CH_3-Al bond by inserting the CH_2 moiety into the Al-H. This reaction scheme needs the breaking of the CH bond of CH_2I_2 on the Al(111) surface as a key step. Yates, et. al. reported the formation of a methylidyne group ($\equiv$C-H) on CH_3I/Al(111)[3] and that the C-H bond is broken on the Al surface. Consequently, $CH_3Al(H)I$ is formed as a result of a cascade of reactions of CH_2I_2 with Al. Although the exact reaction process may be more complicated than considered here, all the key steps are expected to be facile on the surface as discussed here.

It is important to note that through the reaction between alkylhalides and transition metal surfaces the metal-CH_3 bond was formed and the desorption of CH_4, C_2H_6 and hydrogen was exclusively observed in TD experiments.[13,14] This is the striking contrast to the reaction between CH_2I_2 and Al(111) which leads to the desorption of an organoaluminum compound without decomposition of CH_3-Al bond. This shows a different aspect of the surface chemistry of non-transition metals from that of transition metals. To make an surface Al atom as an aluminum compound desorb, there must be a driving force to break the Al-Al metallic bond in the surface and near the surface. Considering that the alkyl groups of alkylaluminum compounds shows strong reactivity as carbanions[1] and the electronegativities of H and I, whose values are 2.1 and 2.5, respectively, are lager than that of Al (1.5), one can recognize the desorbed organoaluminum compound and inorganic aluminum compounds to have negative methyl group, I and H. Especially, the methyl group and I are strong electron attractive groups on the Al surface. As a dry etching process for Al surfaces, the reaction between Cl_2 and Al surfaces has been used.[15] Al reacting with Cl_2 at room temperature results in isotropic etching. Reaction only occurs once the native oxide, which forms a passivating layer to strongly electron negative chlorine attack. Surface Al atoms desorb as $AlCl_3$ or Al_2H_6. Because Al surfaces are liable to discharge electron shown in the low electronegativity, electron attractive groups on Al surfaces attract strongly the electrons in the surface neighborhood and are apt to oxidize Al surfaces. On this dry etching process, the oxidation by the adsorption of negative chlorine breaks the Al-Al metallic bond. As a result, the strong electron attractive groups such as methyl group and I on the Al(111) surface might break the Al-Al metallic bond in the surface layer and bulk by a kind of "oxidation" and form the desorbed aluminum compounds. And indeed the dry corrosion of the Al surface shown in Figure 2 reflects this oxidation process.

3-4 Formation of ethylene.

As described in 3-1 and shown in Figure 1, parent molecules (CH_2I_2) did not desorb from the surface below 1 ML. This implies that the reaction of CH_2I_2 on the surface below 1 ML is different from that on the surface above 1 ML. The desorption of $CH_3Al(H)I$ was observed at 472 K from a very low coverage as shown in Figure 6. This indicates that the main reactions are the decomposition of CH_2I_2 which leads to the precursor of $CH_3Al(H)I$ below 1 ML. As shown in Figure 4 the desorption of $CH_3Al(H)I$ (472 K), $HAlI_2$ (592 K), and AlI (668 K) was already observed at 0.5 ML. These peaks did not increase in intensity so much above 1 ML. On the contrary, the desorption of AlI_3 and ethylene began at 1 ML as shown in Figure 4. TD peaks of ethylene and AlI_3 increased in intensity exclusively above 1 ML. We will discuss this behavior later. These results indicate that the most part of adsorbed CH_2I_2 is reacted with Al below 1 ML to form an aluminum compound layer from which aluminum compounds such as $CH_3Al(H)I$ and AlI desorb.

The following TD experiments were made to get further insight into the ethylene formation and results are shown in

Figure 7. Figure 7A displays the TD spectrum of m/e=27 from the CH_2I_2 of 1.6 ML adsorbed Al(111) surface. Figure 7B shows the TD spectrum of m/e=27 for the surface cooled down to 108 K after the Al(111) surface, on which CH_2I_2 of 1.6 ML was adsorbed at 108 K, was annealed at 164 K for 30 min. While CH_2I_2 did not desorb below 164 K, ethylene desorbed below this temperature as shown in Figure 7A. Although ethylene and CH_2I_2 did not desorb from the surface after subsequent annealing at 164 K as shown in Figure 7B, the peak at 380 K due to AlI_3 increased in intensity compared with that in Figure 7A. Since no desorbed species except ethylene was observed below 164 K, CH_2I_2 molecules reacted on Al below 164 K and changed into a surface compound which lead to the desorption of ethylene and AlI_3.

From the results described above, it is expected that a surface reaction similar to the Simmons-Smith reaction takes place on the Al(111) surface and leads to the desorption of ethylene. In Figure 7 it is noticeable that TD peak intensities due to $CH_3Al(H)I$ (472 K),$AlHI_2$ (580 K) and AlI (655 K) did not change significantly after the annealing treatment. This indicates that the formation of ethylene and AlI_3, which occurs above 1 ML, does not influence the amount and nature of the surface compound formed by the main reaction below 1 ML. The exact chemical identity of the surface compound is not made clear yet, however, the compound has at least a CH_3-Al bond. In the Simmons-Smith reaction between Zn and CH_2I_2, ethylene is formed by the coupling of carbenes

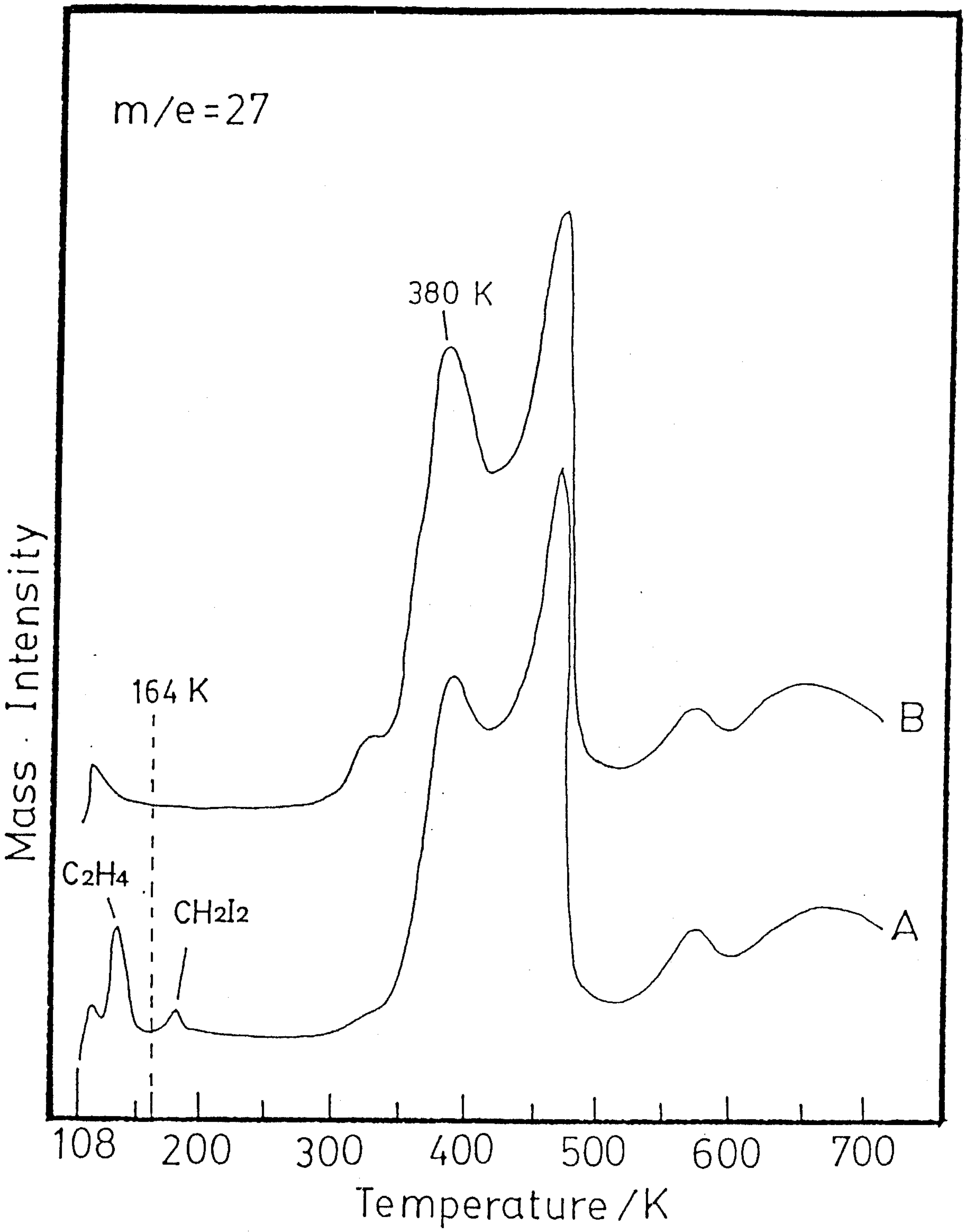

Figure 7. TD spectra of m/e=27 for the CH_2I_2 adsorbed Al(111) surfaces.
A: After the surface was adsorbed by CH_2I_2 to 1.6 ML at 108 K.
B: After A was annealed at 164 K for 30 min.

through a precursor state [I-Zn-CH_2-I] as described before. It is expected that carbene (:CH_2) or its analogue is generated on the Al surface by a similar reaction to the Simmons-Smith reaction. A CH_3-Al bond is formed by the insertion of the CH_2 analogue into a Al-H bond below 1 ML and almost suppressed above 1 ML. In other words, the Al-H bond is necessary to form the surface compound, from which an organoaluminum compound desorbs. If there is not the Al-H bond to react on CH_2 analogue, the CH_2 analogue couples each other and forms ethylene. Thus the formation of ethylene might proceed on the surface compound. This is the reason why ethylene is exclusively formed above 1 ML.

Since ethylene desorbs at lower temperature than CH_2I_2 does and gives a separate sharp desorption peak from the CH_2I_2 desorption peak, the ethylene formation is not simple thermal decomposition in the physisorbed CH_2I_2 layer. To clarify the details of the mechanism of the ethylene formation, we need to identify the surface compound and also the CH_2 analogue by spectroscopic methods. These endeavors will bridge between the surface chemistry and the organometallic chemistry.

4. Conclusions

The reaction between CH_2I_2 and Al(111) was studied extensively by surface analytical techniques, especially AES and TD. Main results are summarized as follows.

1. CH_2I_2 reacts with Al(111) at 108 K. A part of carbon species
formed at this temperature locates beneath the aluminum surface.

2. Below 1 ML, CH_2I_2 does not desorb from the surface. The main reaction of CH_2I_2 on Al(111) is the formation of a surface aluminum compound which involves a CH_3-Al bond; this is formed through the reaction between species containing an Al-H bond and species like a carbene. When the sample temperature is increased organoaluminum compounds like $CH_3Al(H)I$ desorb through the decomposition of the surface compound.

3. The oxidation by the methyl group and iodine on the surface is considered to cause the formation and desorption of aluminum compounds.

4. Above 1 ML, CH_2I_2 desorbs at 190 K from the surface. The main reaction above 1 ML is the formation of ethylene and AlI_3. Not a small amount of CH_2I_2 is consumed by this

reaction. These products desorb at 150 K and around 380 K, respectively. The amount of the surface compound, from which aluminum compounds desorb, does not increase so much above 1 ML. These results suggest that the formation of ethylene from CH_2I_2/Al(111) proceeds by the similar mechanism as the Simmons-Smith reaction.

Studies in this direction will provide useful information on the formation of organometallic compounds over solid surfaces, especially non-transition metal surfaces.

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4. Desorption of Aluminum Hydride from Hydrogen Adsorbed Al(111) Surface

1. Introduction.

Chemisorption of hydrogen on metal surfaces, especially on transition metal surfaces, have been widely studied and a tremendous volume of results has been accumulated.[1]

Although aluminum plays very important role in catalysis and thin film technology, surface chemistry of aluminum is not well understood compared with transition metals. Moreover, the interaction between hydrogen and aluminum is very important in organometallic chemistry because of instability of the Al-H bonds. The character of the bond is electron deficient and is related with the diversity of organo aluminum compounds. For example, triethylaluminum[2] is practically used as Zieglar-Natta catalyst. Due to the high activity of the Al-H bond, $LiAlH_4$ works as a strong hydrogenation reagent and AlH_3 was potential rocket propellant.

Hydrogen chemisorption behavior on aluminum single crystals has already been studied by several group using a variety of surface science technique.[3,4] All these papers reported, however, that the desorption of hydrogen from aluminum single crystal surfaces obeyed zero-order kinetics, i.e. peak top temperatures in thermal desorption (TD) spectra for hydrogen shifted toward higher temperatures with increasing amount of adsorbed hydrogen. This desorption behavior contrasts with the hydrogen desorption from transition metal surfaces in which the desorption kinetics is second-order, i.e. peak tops temperature in TD spectra for hydrogen shift toward lower temperatures with increasing amount of adsorbed hydrogen[5]. The equation of Redhead, which is based on desorption kinetics, for second-order desorption is expressed as follows[5]:

$$E/RT_m^2 = (n_0 \nu /B)\exp(-E/RT_m)$$

where n_0 and T_m are the initial coverage of the adsorbate and the temperature of TD peak top, respectively. The values of E, R, ν and B are the activation energy for the desorption, gas constant, frequency factor and the heating rate of a surface, respectively. This equation indicates that T_m decreases with increasing n_0 in the case of second-order desorption. This second-order desorption suggests that the recombination of hydrogen atoms on the surfaces is the rate determining step. The zero-order desorption of hydrogen from aluminum single crystal surfaces suggests that the mechanism of desorption is different from the intuitively understandable one mentioned above.

Thus we investigated chemisorption and desorption behavior of hydrogen on an Al(111) surface by detailed analysis of TD spectra. In the course of this experiment, we found that an aluminum hydride desorbed from the surface. This is the first report on desorption of metal hydride from hydrogen adsorbed metal surfaces.

2. Experimental.

The experiments were performed in two UHV chambers. The chamber A (section 2.) was used to investigate TD for a hydrogen adsorbed Al(111) surface. An Al(111) (7x7x1 mm) surface was cleaned by repeated cycles of Ar^+ bombardment at room temperature and annealing at 723 K. Cleanness and ordering of the surface was confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED).

The experiments for an Al films deposited on the Mo(111) surface, which were carried out in order to estimate the amount of the desorbed aluminum hydride, and XPS measurements for the hydrogen adsorbed Al(111) were performed in the chamber B (section 2.). The mounting of the Mo(111) single crystal to a manipulator was similar to that of the Al(111) single crystal. (section 2)[6,7] The cleaning of the Mo(111) surface was performed by the cycle of Ar^+ bombardment (5 kV, 20 μ A) at room temperature and annealing at 1073 K. The deposition of Al onto the surface was reproducibly controlled by resistively heating a shielded evapolation source consisting of a 0.5 mm diameter Ta wire wrapped around Al wire (99.999 %). AES analysis (Al(LMM, 68 eV) and Mo(MNN, 186 eV)) of the deposited overlayer confirmed that pure Al was deposited on the Mo(111) surface. Al Kα (hν = 1486.6 eV) was used as an excitation source. The detail description for the Al films deposited on the Mo(111) surface will be seen in section 6 and an our paper.[7]

Both the Al(111) single crystal and the Al films deposited on the Mo(111) surface were cooled down to indicated temperatures below room temperature before the exposure to hydrogen. The dissociative adsorption of hydrogen molecule can not occur on Al surfaces because Al does not have d-electron. For this reason, hydrogen has to be dosed as atom in order to make hydrogen atom adsorb on Al surface. Hydrogen atom was generated by thermal dissociation of introduced H_2 (5×10^{-7} Torr) by a heated tungsten filament (0.5 mm diameter) at ca. 2000 K. After the hydrogen (Nippon Sanso, 99.99999 %) of 3 atm in the gas introduction systems cooled by liquid N_2 was reduced to 5×10^{-7} torr by leak valves, the hydrogen was introduced into the UHV chambers. This is because of reducing the impurities in the introduced H_2 gas. The amount of adsorbed hydrogen was controlled by changing heating time of the filament and determined by the TD peak area of m/e = 2 (H_2^+). The filament was set at the distance of about 5 mm above the surface. Temperature of the sample was kept at indicated temperatures during the exposure to hydrogen atoms.

In the thermal desorption experiment, the sample was then heated from the adsorption temperatures to 730 K at a heating rate of 10 K/s. The desorbed species were detected by means of the quadrupole mass spectrometers in line of sight. The ionization energy of the mass spectrometers was 70 eV. A digital oscilloscope (SONY Tektronix, Type 11402) was also connected to the mass spectrometers. Thus the mass spectra of desorbed species at a certain temperature during TD experiments could be recorded by a high rate scanning of the mass number. For XPS, Al Kα was used as the excitation light (the incident angle is a 32°).

3. Results and Discussion.

3-1. The desorption of an aluminum hydride.

Figure 1A shows TD spectra of m/e = 2 (H_2^+) at various hydrogen coverages. Desorption peaks were observed at ca. 340 K. Coverage of hydrogen on Al(111) surface was estimated by TD experiments of H_2^+ (m/e = 2). Areas of TD peaks for H_2^+ were constant above exposure time of 6 min. Since the exact concentration of hydrogen atoms, which were generated by the tungsten filament, was not determined, we used the heating time of the tungsten filament as the measure of the exposure time. Sharp (1 x 1) LEED spots were observed at whole exposure times from 0 min to 6 min. The electron diffraction of hydrogen adatom is hard to arise because hydrogen atom is too small to diffract electron. As a result, sharp (1 x 1) LEED spots were the LEED pattern for Al(111) and could not give the informations for the adsorbed hydrogen to us. Thus the amount of hydrogen which was adsorbed on the surface by the exposure time of more than 6 min, that is to say, the saturation coverage of hydrogen was defined as one monolayer (

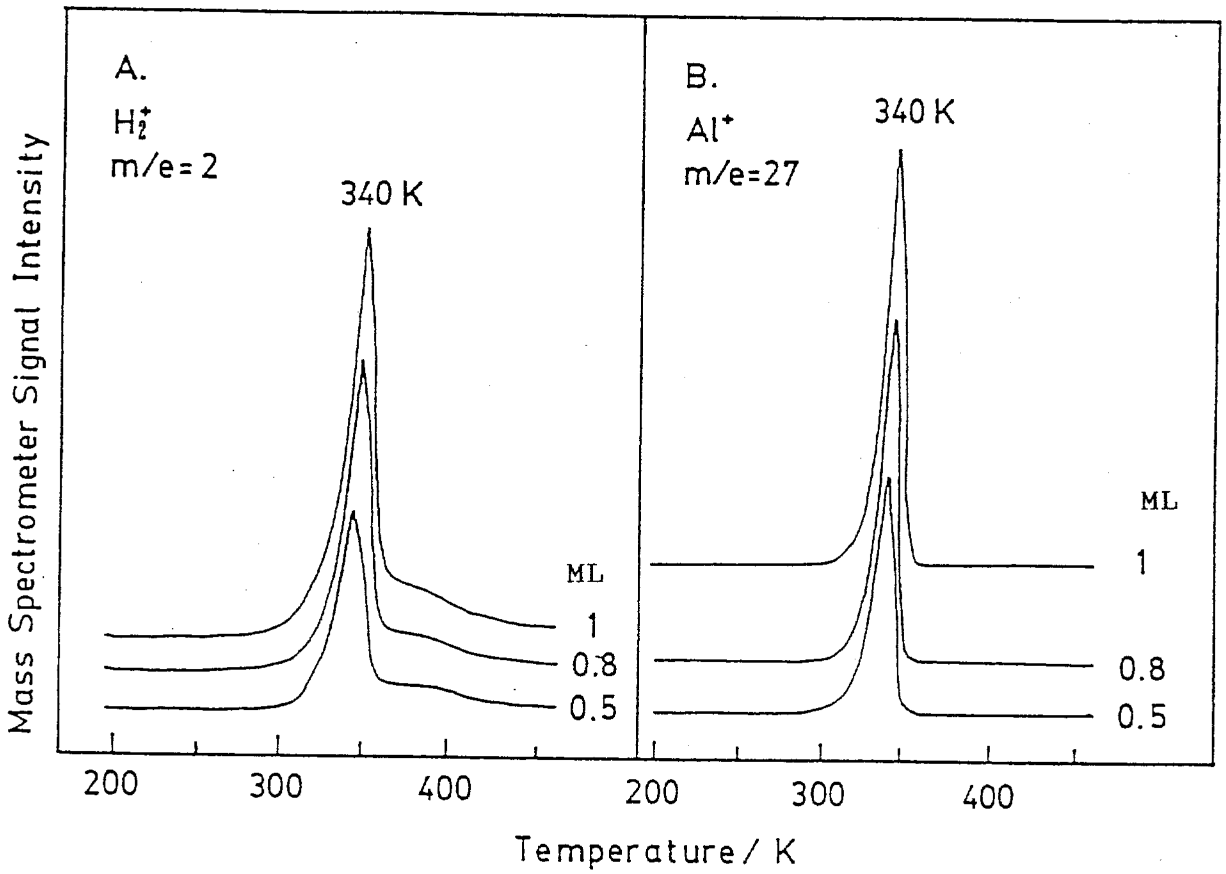

Figure 1. TD spectra of H_2^+ (m/e=2) (A) and Al^+ (m/e=27) (B) from hydrogen adsorbed Al(111) surfaces at various hydrogen coverage.

1 ML) coverage of hydrogen.

The peak tops shifted toward higher temperatures with the increase of hydrogen coverage. Furthermore, these peaks had common leading edges. This means that TD for m/e = 2 obeys the zero-order desorption. In Figure 1B, TD spectra for m/e = 27 under the same experimental condition are also shown. The TD peaks of m/e = 27 are due to Al^+ (m/e = 27) because m/e = 26 was not detected at all. If the TD peak of m/e = 27 results from the mass fragments of hydrocarbons like $C_2H_3^+$ (m/e = 27), the signal of m/e = 26 ($C_2H_2^+$) has also to be detected. As a result, the peaks of Al^+ were detected at ca. 340 K, where TD peaks of H_2^+ were observed. The intensity of TD peak of H_2^+ is by about a hundred times higher than that of Al^+ for the same coverage of hydrogen. The transmission factor of the mass spectrometer was calibrated by measuring the relative sensitivity for H_2, He (m/e = 4), Ne (m/e = 20), and Ar (m/e = 40). The ratio of the transmission factors for m/e = 2 and m/e = 27 was 10/1. Taking into account the difference of the transmission factors, TD peak intensity of Al^+ is not negligible compared with that of H_2^+. This means that the amount of Al^+ is not a spurious trace. Because Al atom is not likely to desorb at this temperature, Al atom on the surface desorbs as an aluminum compound. To estimate the amount of the desorbed aluminum compound, the TD and AES experiments for a hydrogen adsorbed Al film deposited on the Mo(111) surface were performed. The TD experiments for the Al film (2 atomic layers), on which the hydrogen of 1 ML was adsorbed at 250 K, revealed the TD peak of Al^+ to be observed at around 370 K. After the desorption of the aluminum compound, about 30 % of Al atoms on the first surface layer were recognized to decrease by the AES measurements (see section 6).[7] This result is indicative of the desorption of the much aluminum compound from hydrogen adsorbed Al surfaces. As shown in Figure 1A, a shoulder at around 370 K in TD of H_2^+ does not have a corresponding shoulder in TD spectra of Al^+ at this temperature. This suggests that the shoulder at ca. 370 K is due to desorption of H_2.

The line shape of the TD spectrum for H_2^+ resembles that of Al^+ as shown in Figure 1. Furthermore, the coverage dependence of the peak shifts and leading edges of TD peaks for H_2^+ and Al^+ coincide completely. The peak intensities of TD spectra for H_2^+ and Al^+ at around 340 K shown in Figure 1 as a function of the exposure time to hydrogen atom is shown in Figure 2. The TD peak intensities were almost constant above 6 min because the surface saturated by hydrogen was accomplished at this exposure time as mentioned above. Figure 2 reveals that the intensity ratio between the TD peaks for H_2^+ and Al^+ is almost constant at the whole exposure times. Taking account of these facts, TD peaks of H_2^+ and Al^+ at around 340 K are expected to result from the fragments of a single desorbed species. As a result, aluminum hydride is considered to desorb at this temperature. To our knowledge, this is the first observation of the desorption of metal hydride from the hydrogen adsorbed metal surface.

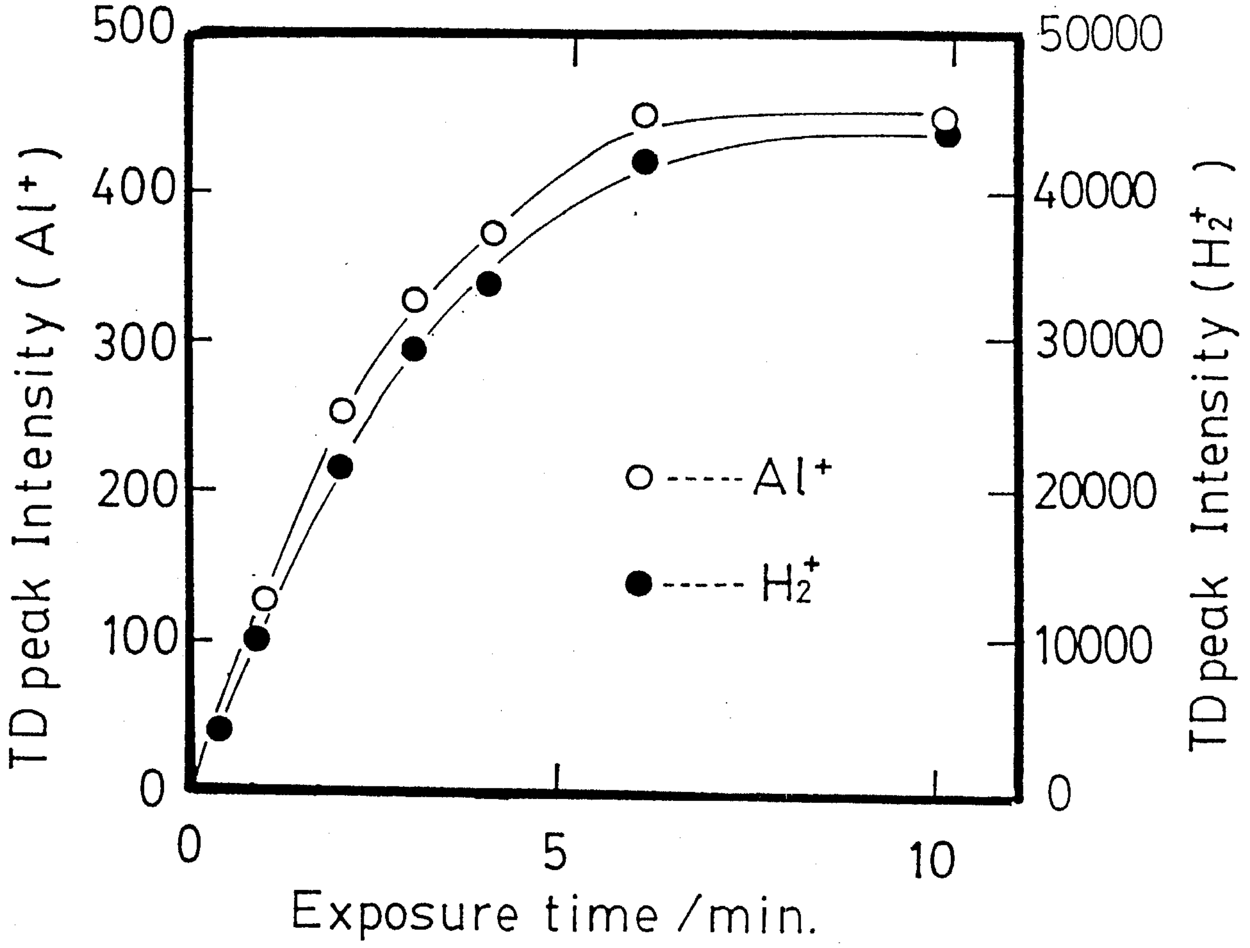

Figure 2. TD peak intensities of H_2^+ and Al^+, which were determined by peak areas of Figure 1, as a function of the exposure time to hydrogen atom at 150 K.

To get further insight into the desorbed species, a mass spectrum of the desorbing species from the hydrogen adsorbed Al(111) surface (150 K, 0.5 ML) was measured at 330 K while the sample temperature was raised by the same condition as the ordinary TD experiment. This snapshot mass spectrum was measured by scanning mass number from m/e=25 to m/e=32 with a mass scan rate of 125 amu/s and stored in the digital oscilloscope. The mass spectrum thus obtained at 330 K is shown in Figure 3 after subtracting a background spectrum. The background spectrum was measured at 150 K, immediately before the start of the temperature rise.

Signals of m/e = 27, 28, 29, 30 and 31 were detected at this temperature. The intensity ratio of these signals clearly indicate that these peaks are neither due to hydrocarbons nor CO. Each peaks are assigned to Al^+, AlH^+, $AlH_2{}^+$, $AlH_3{}^+$ and $AlH_4{}^+$ respectively. The split of the AlH^+ peak (m/e = 28) was an artifact caused by the background subtraction of CO (m/e = 28) peak, which had the intensity of about 30 % of that of AlH^+. This again indicates the desorption of much aluminum compound because CO is a main resident gas in UHV chambers. Furthermore, signal of m/e = 60 ($Al_2H_6{}^+$), which was not shown in Figure 3, was detected at this temperature. The mass signal above m/e = 61 was not detected in this experiment. The intensity of the signal for m/e = 60 was about half that for m/e = 30. AlH_3 (alane) and its dimer, Al_2H_6 (dialane), have been reported to exist under vacuum.[8] Electron deficient compounds such as bolane (BH_3) and alane are liable to form

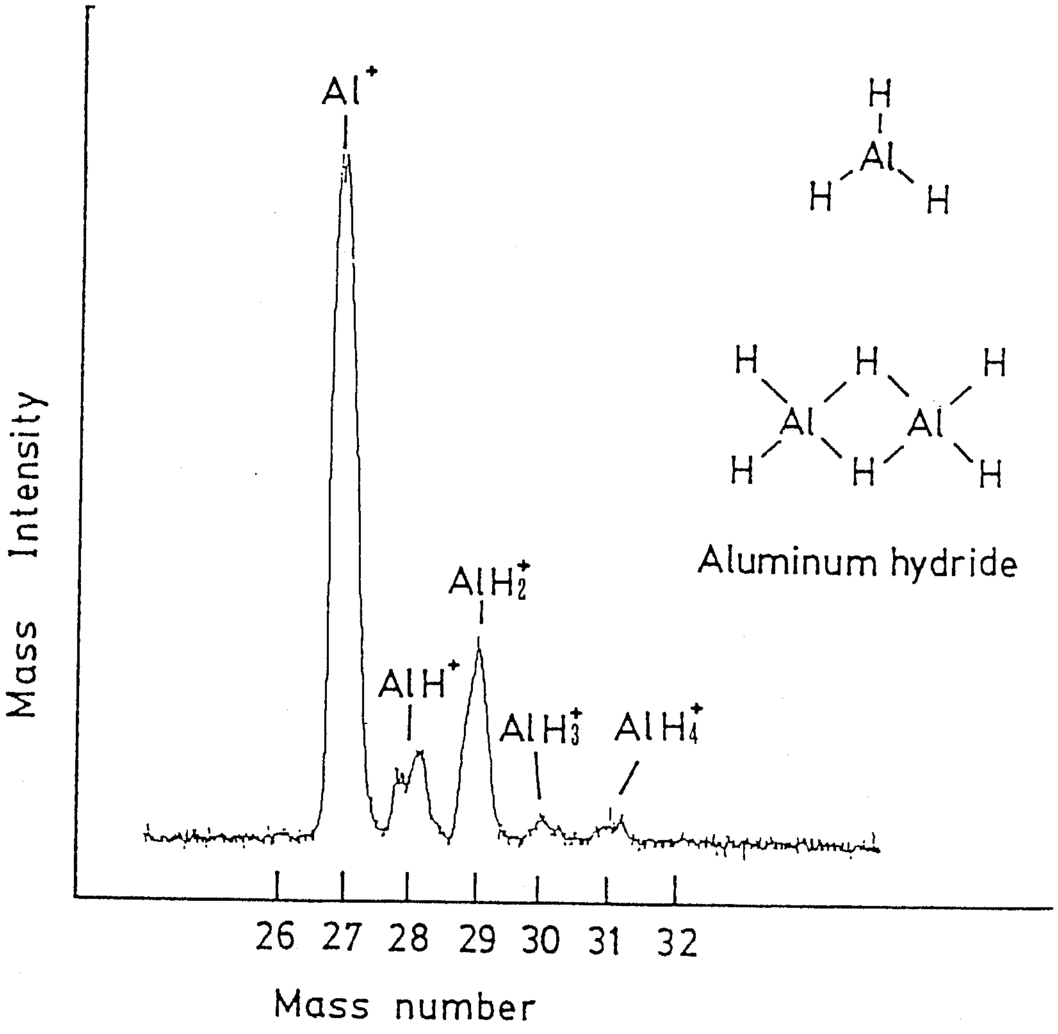

Figure 3. The mass spectrum of desorbed species at 330 K when 0.5 ML H/Al(111) was heated at the rate of 10 K/s. Scan rate was 125 amu/s.

the dimers by the three-center bonding through the bridging hydrogen.[9] These aluminum hydrides are, however, very unstable and easily decompose into Al and H_2[10]. Because of its inherent instability the mass spectroscopic fragmentation patterns of the aluminum hydrides have never been measured. On matrix isolation method, even the collision of aluminum hydride to the matrix at extremely low temperature decomposes aluminum hydride almost into Al and H_2. For this reason, there is no spectroscopic data for aluminum hydride although many studies have ever attempted to get its spectroscopic data.[11] Thus, we can not only determine the exact molecular formulas for the desorbing species from the mass fragment pattern. TD peaks of Al^+ give the key to expect the desorbed species to us. The TD peak of Al^+ shown in Figure 1 is a single peak. This indicates that the aluminum hydride of a single component desorbs from the hydrogen adsorbed Al(111) surface. Considering the largest mass number among detected signals to be m/e = 60 due to $Al_2H_6^+$, only Al_2H_6 is expected to desorb. However, we can not simply determine whether only Al_2H_6 or the mixture of AlH_3 and Al_2H_6 desorbs. This is because these two aluminum hydride are due to a same aluminum hydride.

One can recognize the mass signal of Al^+ to be main signal in Figure 3. In the quadrupole mass spectrometer, desorbed species were ionized by electron beam. Because aluminum hydride liable to decompose as mentioned above, many part of the desorbed aluminum hydride might be decomposed into Al and H_2 in the mass spectrometer where the aluminum hydride is ionized by the electron beam.

From all the results mentioned above, we conclude that at least a large part, perhaps almost all of adsorbed hydrogen desorbs at around 340 K as aluminum hydrides such as Al_2H_6 or AlH_3. If aluminum hydride and H_2 desorbed simultaneously at around 340 K, the results shown in Figure 1 and 2 would lead to that aluminum hydride and H_2 had the same activation energy for the desorption. Generally, It is impossible that several desorbed species have the same activation energy for the desorption. It is expected that the desorption of aluminum hydrides relates with zero-order desorption kinetics.

3-2. The XPS measurements of the hydrogen adsorbed Al(111) surface.

The electronic state of Al atom on the surface might be influenced through the interaction with hydrogen. We investigated the inner shell of Al on the hydrogen adsorbed Al(111) surface by means of XPS. In order to sensitively observe the change of electronic state of Al, XPS measurements was performed at the photoemission angle of a 70°. Generally, the information for surface increases with increasing the photoemission angle on photoelectron spectroscopy. After the kinetic energy of photoelectron from the surface was analyzed, the binding energy was defined by the Fermi edge of the spectrum.

A XP spectrum for the Al 2p of the clean Al(111) surface is shown in Figure 4A. Figure 4B displays the XP spectrum for the hydrogen adsorbed Al(111) surface at 110 K, on which hydrogen of 1 ML was adsorbed at 110 K. The peak top of spectrum B does not shift compared with spectrum A. After the measurement of spectrum B, the sample was heated to 220 K, at which the desorption of aluminum hydride was not observed, and annealed for 10 min at this temperature. After the sample was cooled down to 110 K, the XP spectrum shown in Figure 4C was measured. One can recognize the peak top of spectrum C to shift slightly toward higher binding energy than that of spectrum A and B. This suggests the charge transfer from the Al surface to the adsorbed hydrogen atom and the formation of Al species which has positive charge with increasing surface temperature. Electron population analysis of AlH_3 gives a net charge of + 0.31 on an Al atom and -0.10 on a hydrogen atom.[12] As a result, the precursor state for the desorbed aluminum hydride might be formed with increasing the surface temperature.

In this study, it was confirmed that the desorption of aluminum hydride from the hydrogen adsorbed Al(111) surface. It is a further subject to investigate the formation and desorption mechanism of aluminum hydride.

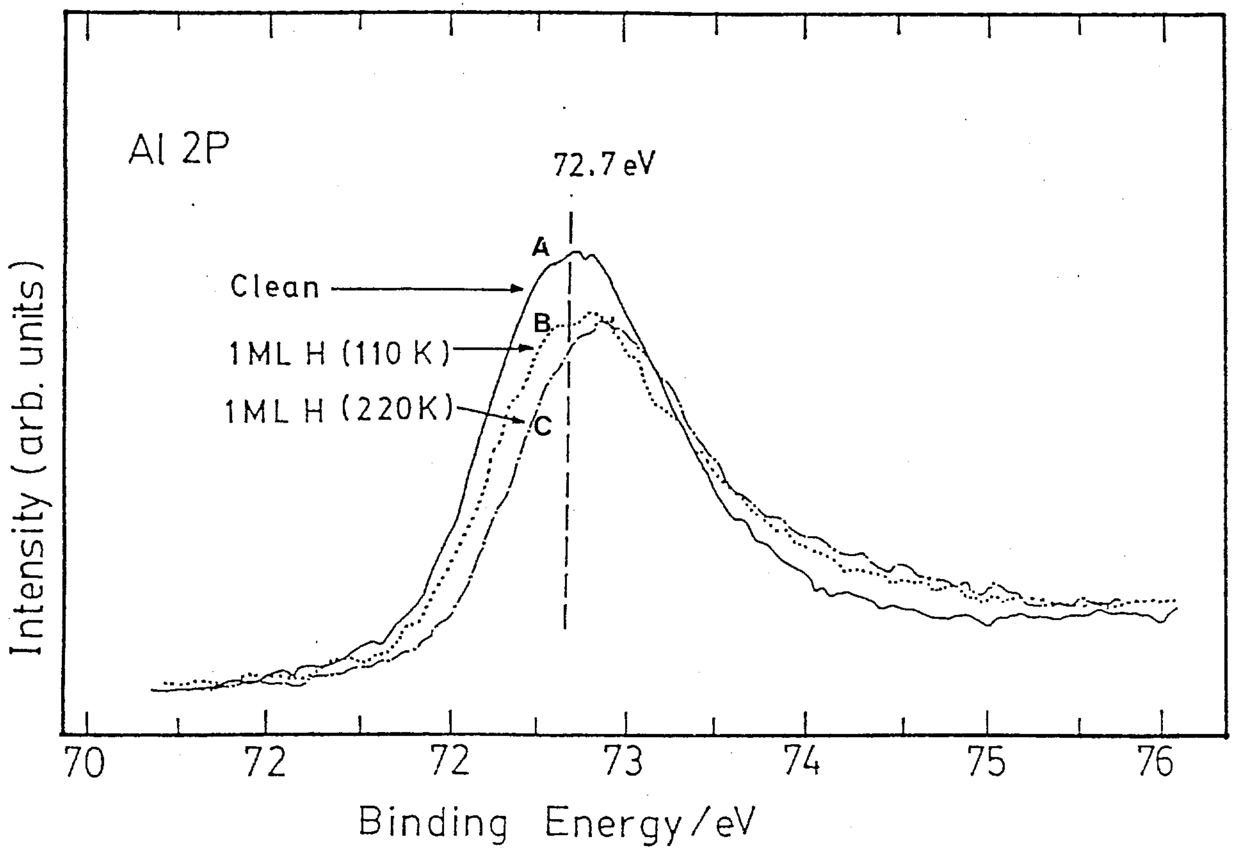

Figure 4. XP spectra for the clean Al(111) surface at 110 K (A), the 1 ML hydrogen adsorbed Al(111) surface at 110 K (B) and 220 K (C).

5. Conclusions.

1. The desorption of much aluminum hydride from the hydrogen adsorbed Al(111) surface was observed at around 340 K for the first time. Only aluminum hydride is expected to desorb from the surface.

2. The desorbed aluminum hydride was suggested to be a single component such as Al_2H_6 or AlH_3.

3. XPS measurements were indicative of the charge transfer from the Al atom on the surface to adsorbed hydrogen with increasing surface temperature. This suggested that the bonding state of Al-H changed by the process of the surface reaction.

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5. The formation and desorption mechanism of aluminum hydride on hydrogen adsorbed Al(111) surface

1. Introduction

The hydrogen adsorbed Al surfaces, which is the adsorption of the simplest atom on the simplest sp-metal surface, have ever been studied by means of TD or HREELS.[1,2,3] However the desorption of aluminum hydride such as Al_2H_6 or AlH_3 from the surface has never been been unknown. This is because the desorption of hydrogen molecule from hydrogen adsorbed metal surfaces is a common sense which has been adopted in transition metal surfaces. At the view point that aluminum hydride desorbs from hydrogen adsorbed Al surfaces, this system have never been investigated.

In section 4, TD was mainly used to investigate the hydrogen adsorbed Al(111) surface. Although these TD experiments offered the informations for the desorption manner, the desorbed species and the amount of the desorbed aluminum hydride,[4] it is difficult to consider the mechanism for the formation and desorption by only these TD experiments. Thus, we observed the electronic states for the hydrogen adsorbed Al(111) surface by means of ultraviolet photoelectron spectroscopy (UPS) in order to investigate the behavior on the surface. The electronic structures for hydrogen adsorbed metal surfaces have been studied on many transition metals or semiconductor surfaces such as silicone, gerumanium and so on. However the electronic structure for the hydrogen adsorbed Al surface has never been investigated.

UPS is a excellent method to observe the detail structure of valence band. Because chemical bond takes place through valence orbitals, the UP spectrum and interpretation for a simple-looking chemical bond are sometimes complex. As a result, the eigen values of the molecular orbitals for hydrogen adsorbed Al model clusters were calculated by the first-principles (ab initio) to assist the interpretations for the UP spectra on hydrogen adsorbed Al(111) surfaces. In addition, molecular AlH_3 (alane) and Al_2H_6 (dialane) were also calculated. There is no spectroscopic results for these aluminum hydride because these compounds are unstable as mentioned in before section. The calculations for AlH_3 and Al_2H_6, which are considered as the desorbed species from the hydrogen adsorbed Al(111) surface, might give available informations to us. The first-principles calculations for Al model clusters will be hard to offer correct quantitative value as a material characteristic, for example, conductivity or work function, but it will give the qualitative informations for local matters as chemical bond to us.

In this study, the electronic states of aluminum-hydrogen bonds and the formation and desorption of aluminum hydride are discussed by both the experimental results and calculations. These results revealed that the desorption of aluminum hydride from the hydrogen adsorbed Al surface proceeds through several dynamic processes although this system is simple-looking. The charge transfer from the Al surface tho the adsorbed hydrogen and the surface structure of Al(111) are expected to cause the formation and desorption od aluminum hydride from the hydrogen adsorbed Al(111) surface.

2. Experimental

The experiments were performed in a stainless-steel UHV chamber B (Figure 3,4 in section 2). The details for the experiments are described in before section.

All of the UPS measurements were carried out with He(I) (hν = 21.2 eV) light whose incident angle is a 30°. The photoemissions along the Γ K azimuth of the Brillouin zone for the Al fcc single crystal were measured at the angle θ which could be set independently. The resolution of the analyzer for UPS was set at 40 meV. For the X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) measurements, Al Kα (hν =1486.6 eV) was used. AES spectra were measured by integral mode.

3. The first-principles (Ab initio) calculations

The first-principles calculations were carried out with the DMol software package,[5] which calculated variational self-consistent solutions to the local density functional (LDF) theory.[6] The total electronic energy can be written as a functional of the density in the form

$$E[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho] \qquad (1)$$

where $T[\rho]$ is the kinetic energy of a system of non-interacting particles of density ρ, $U[\rho]$ is the classical electronic energy due to the Coulomb interactions, and $E_{xc}[\rho]$ includes all many-body contributions to the total energy, in particular, the exchange and correlation energies. The total density may be decomposed into single particle densities that are related to single particle wave functions (molecular orbitals) by:

$$\rho(r)=\Sigma\,|\,\phi_i(r)\,|^2 \qquad (2)$$

where the sum goes over all occupied molecular orbitals (MO), ϕ_i. The density from this expression is also known as the charge density. Using the decomposition of Eq.(2) the conditions to variationally minimize $E[\rho]$ with respect to ρ lead to effective one-particle Schodinger equations of the form:

$$[-1/2\nabla^2 + V_{eff}(r)]\,\phi_i = \varepsilon_i\phi_i \qquad (3)$$

The first term is the kinetic energy operator for the electrons. The second an effective potential, which is taken by LDF theory to be the sum of the Coulomb potential and the potential arising from exchange and correlation.

To solve these equations, clearly, the exchange-correlation energy, E_{xc} requires approximation. A simple and, as it turns out, surprisingly good approximation is the so-called local density approximation. This uses the known many-body energy, $\varepsilon(\rho)$, of an electron in a homogeneous, interacting electron gas of density ρ. This first-principles result can be used to approximate the inhomogenious case by setting:

$$E_{xc}[\rho] \doteqdot \int \rho(r)\varepsilon[\rho(r)]dr \qquad (4)$$

As it turns out, this is particularly appropriate in systems like metals, where the electron density is reasonably well approximated by the electron gas. With this approximation, the effective potential in the LDF equations (3) can be evaluated explicitly.

In the next step, which is numerically the most demanding, the differential equations (3) are solved. In the DMol, program, this is accomplished by first expanding the molecular orbitals as linear combinations of atomic orbitals:

$$\phi_i = \Sigma C_{ij}\chi_j \qquad (5)$$

The atomic orbitals χ_j are called the atomic basis set, and C_{ij} are the MO expansion coefficients. In general LDF method, the molecular orbitals are expressed by the linear combinations of plane waves. Although MO can be easily calculated by LDF method based on plane waves, it can not immediately be determined which of the atomic orbitals the calculated MO is due to because a plane wave is a function of wave vector. On the other hand, the MO can be attributed to atomic orbitals in the DMol program.

In this study, AlH_3 (alane), Al_2H_6 (dialane) and hydrogen adsorbed Al clusters were calculated by the DMol program. The geometries for AlH_3 and Al_2H_6 which is based on the results by Lammertsma et al.[7] are shown in Figure 1. These geometries were determined by the total binding energies (AlH_3 : -10.79 eV, Al_2H_6 : -21.59 eV) where these molecules were the most stable. The calculations such as the binding energies or vibrational frequencies for AlH_3 and Al_2H_6 were in good agreement with the results which were calculated by the GAUSIAN88 and GAMESS.[7,8] An Al_{10} cluster shown in Figure 1, which is composed of seven Al atoms at the first layer and three Al atoms at the second layer, was used as the model cluster. This cluster model is frequently used to calculate the adsorption on f.c.c. (111) surfaces and the most basic unit. Giving the character of metal surface to the Al_{10} cluster, quasi-valence bands were introduced into this cluster.

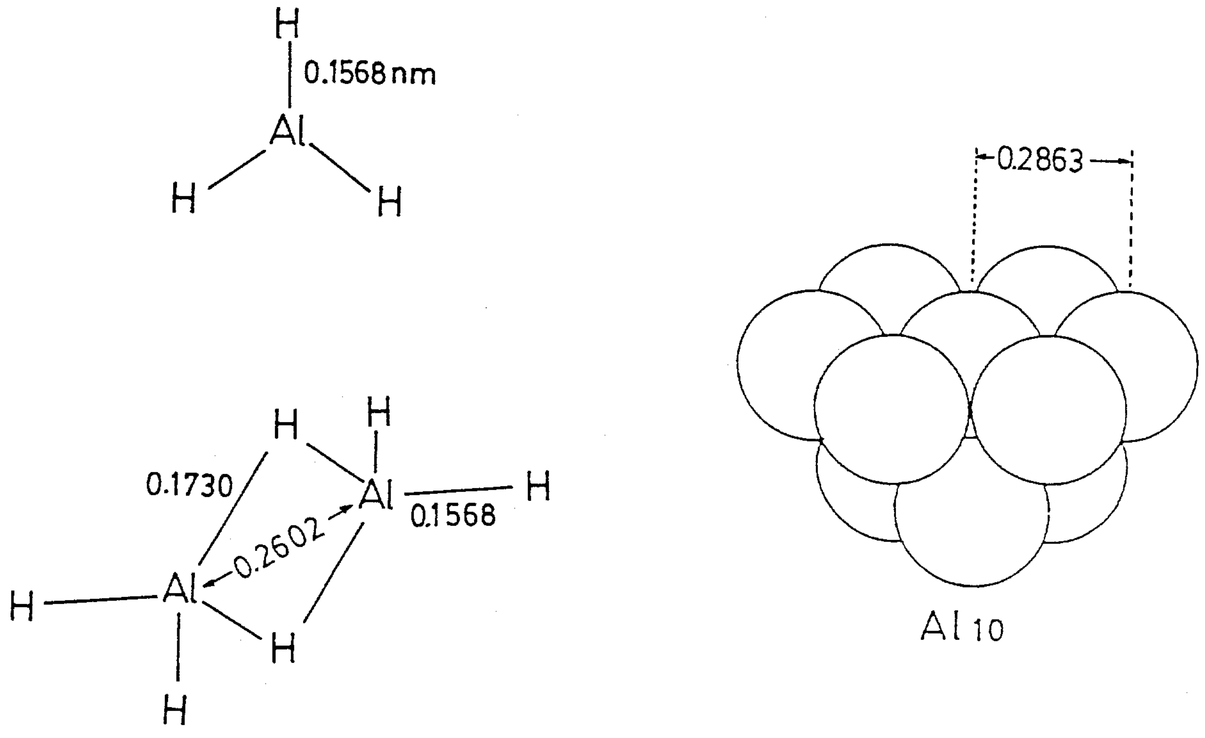

Figure 1. The geometries of AlH_3, Al_2H_6 and Al_{10} model cluster for the first-principles calculations.

4. Results.

4-1. The adsorption of hydrogen atoms at 110 K.

The electronic state of the hydrogen adsorbed Al(111) surface was investigated at the adsorption temperature of hydrogen atom (110 K). Figure 2A shows the UP spectrum at the photoemission angle θ = 10° for the Al(111) clean surface. A broad peak at around 7 eV below the Fermi level originates in the 3s orbital of Al and is due to the direct interaction which is photoexcitation process along Γ K azimuth of the Brillouin zone for Al fcc structure.[9,10] The peak at 10 eV results from the resident Ar which could not be removed from the surface by annealing.[11] One recognizes a flat curve in Figure 2A due to the sum of the Al sp emission and the smooth secondary back ground. The work function ϕ for the clean surface which is obtained by this UP spectrum is a 4.30 eV. This is the adequet value for clean Al(111) surface.

The UP spectrum (photoemission angle θ = 10°) for the Al(111) surface, on which hydrogen atoms of 1 ML were adsorbed at 110 K, is shown in Figure 2B. The change of work function ($\Delta\phi$ = + 0.29 eV) was observed after the adsorption of 1 ML hydrogen at 110 K. This is indicative of hydrogen adatoms which have negative charge. Figure 2C displays a difference spectrum between Figure 2B and 2A. The peak at 5 eV in the spectrum C is due to the local bonding state of the Al-H bond. The states of the local metal-H bonds on many hydrogen

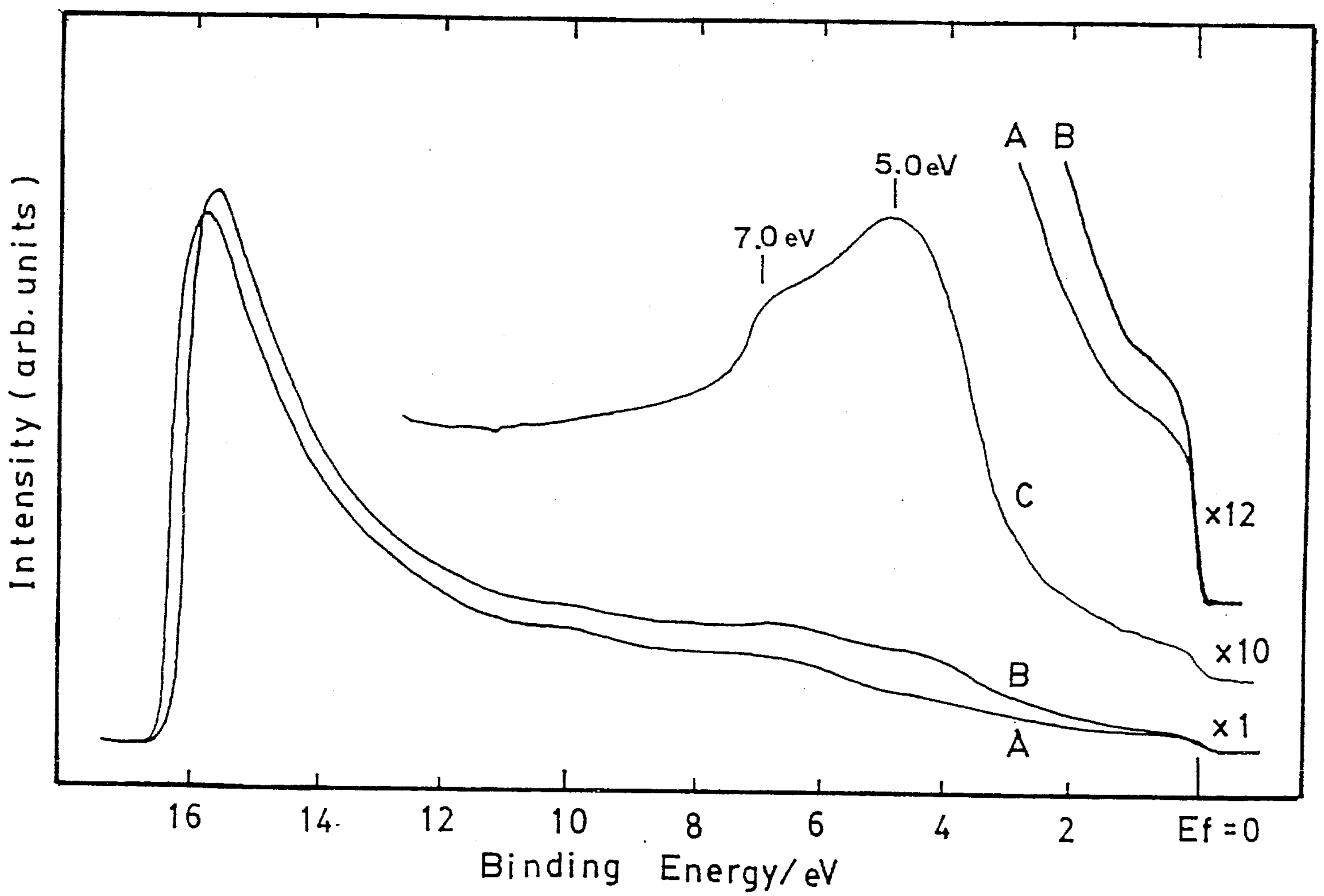

Figure 2. The UP spectrum for the hydrogen adsorbed Al(111) surface.
A: Clean surface. B: The surface on which hydrogen of 1 ML was adsorbed at 110 K. C: The difference spectrum of B and A (B-A).

adsorbed metal surfaces appear at around 5 eV below the Fermi level.[12] One can recognize a shoulder peak at 7 eV below the Fermi level in the spectrum C. At the UP spectra for a hydrogen adsorbed Si(111) surface, the peak at 12.0 eV below vacuum level to add to the peak at 9.8 eV which was due to the local bonding state of the Si-H bond were observed.[13] Self-consistent theory expected that the peak at 12.0 eV reflected the enhancement of the Si 3s-like band enhanced by hydrogen chemisorption on the surface layer.[13,14] Whether this conforms to the peak at 7 eV for the hydrogen adsorbed Al(111) surface is a matter for argument because silicon is not non-transition metal but semicondoctor. Furthermore, Figure 2C shows the states at around 9 eV and below 4 eV. These results indicate that the bonding states at least more than four appear on the hydrogen adsorbed Al(111) surface at 110 K. The line shapes of the difference UP spectra for the hydrogen adsorbed Al(111) surface were almost identical even if the amount of the adsorbed hydrogen adatom was varied from 0.2 ML to 1.0 ML.

The photoemission angle dependence of the difference UP spectra is shown in Figure 3. These spectra were obtained after subtracting the UP spectrum for the clean Al(111) surface at the indicated photoemission angle θ from the UP spectrum for the hydrogen adsorbed Al(111) surface (110 K) at the angle. In the difference spectrum at $\theta = 30°$, a negative peak appears between the Fermi level and around 2 eV. This is because the surface state on nthe clean Al surface vanishes for hydrogen adsorption on the Al(111) surface. The

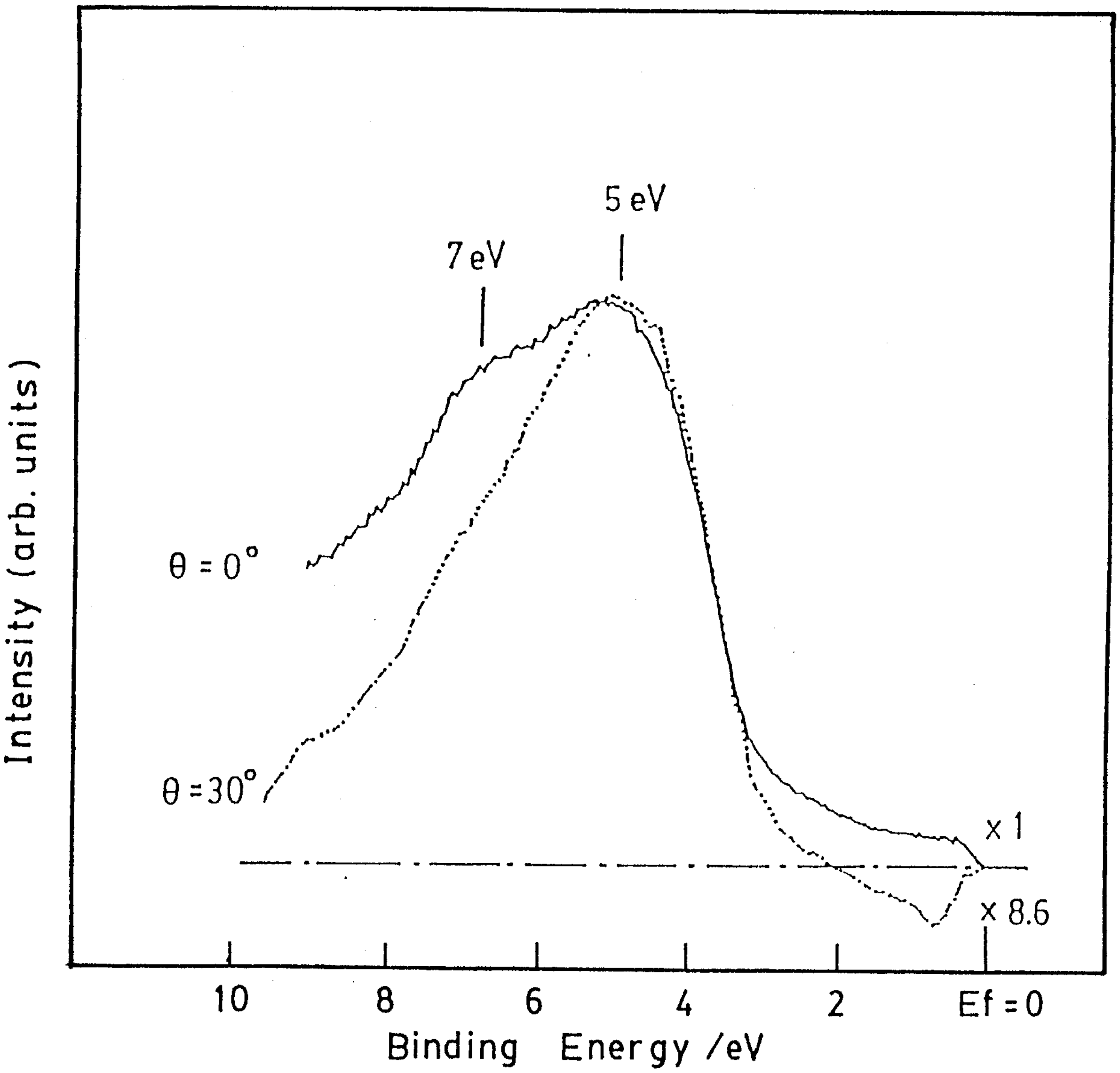

Figure 3. The analyzer angle (θ) dependence of the difference UP spectrum for the hydrogen of 1 ML adsorbed Al(111) surface at 110 K.

surface state for the clean Al(111) surface is observed from the Fermi level to around 2 eV at $\theta = 30°$ but can hardly be recognized at $\theta < 20°$ because of the strong intensity of the Al bulk's valence band.[15] The states below 4 eV and at 7 eV ($\theta = 30°$) is relatively smaller in intensity than that of $\theta = 0°$. Considering the informations of bulk to increase with decreasing the photoemission angle θ , these two states are expected to have relation to the bulk.

4-2. The change of Al-H bond

Figure 4 shows the temperature dependence of the difference UP spectra for the hydrogen adsorbed Al(111) surface. Each spectrum at $\theta = 10°$ was measured at 100 K~ 110 K after the surface on which hydrogen of 1 ML was adsorbed at 110 K was kept at the indicated temperatures for 10 min. The difference spectra were obtained after subtracting an UP spectrum (photoemission angle $\theta = 10°$) for the clean surface ($\theta = 10°$) from the spectra for the hydrogen adsorbed surface. At the indicated temperature in Figure 4, the desorption of aluminum hydride was not observed. As shown in Figure 4, the intensities for the states at around 5 eV, 7 eV and 9 eV increased with increasing the anneal temperature. On the contrary, the intensity for the state between the Fermi level and 3 eV decreased with increasing the anneal temperature. These results suggest that the increase of the

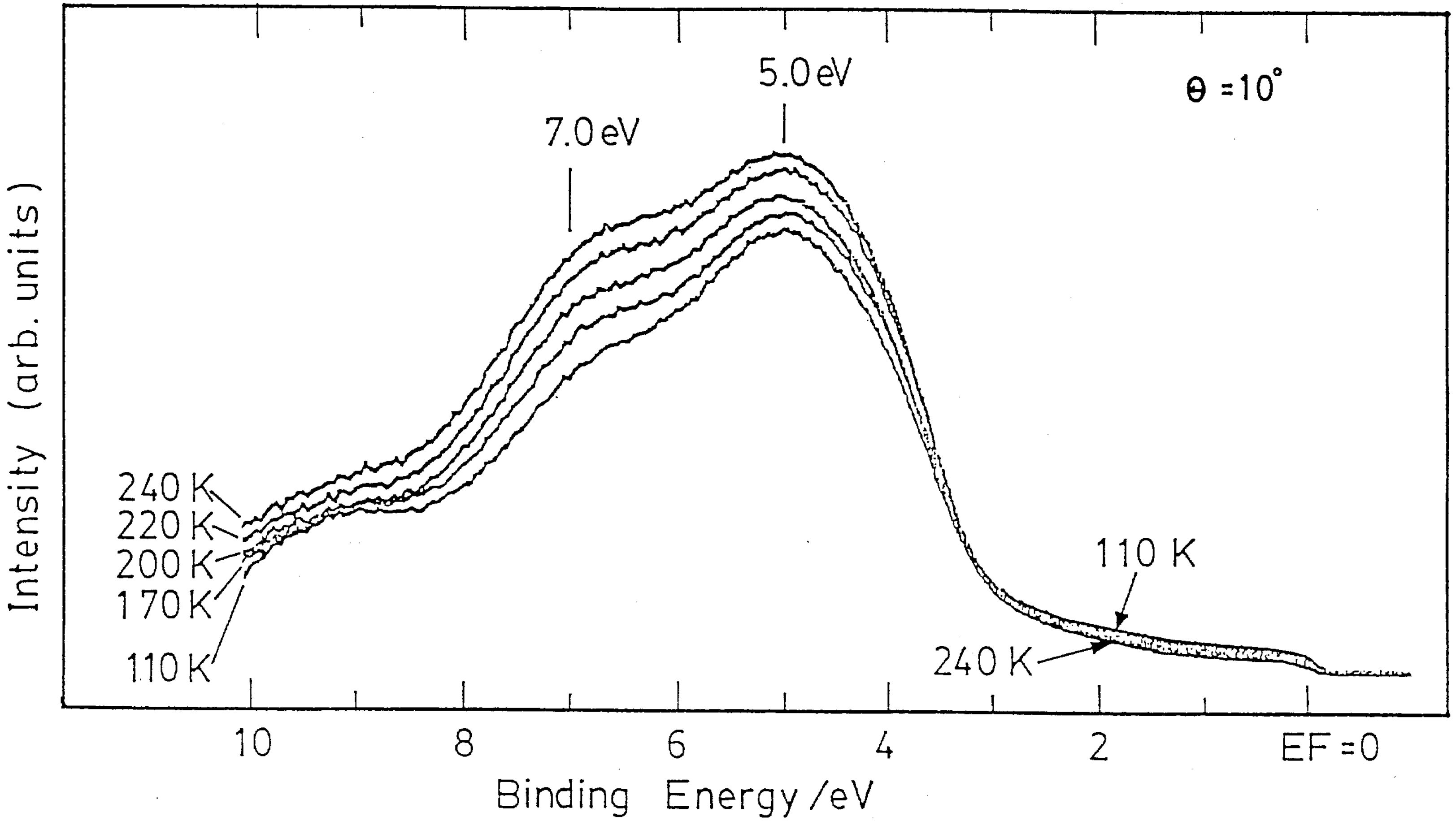

Figure 4. The temperature dependence of the difference UP spectrum for the hydrogen of 1 ML adsorbed Al(111) surface.
UPS measurements were carried out after the surface on which hydrogen of 1 ML was adsorbed at 110 K was kept for 10 min at the indicated temperatures.

surface temperature changes the electronic state of the Al-H bond.

The state below 3 eV in Figure 4 is expected to result from the Al valence band. As a result, the observation for Al LMM AES transition is likely to give the informations for this state to us. Figure 5A displays an integrated AES spectrum for the clean Al(111) surface at the analyzer angle $\theta = 55°$. All of AES spectra were measured at $\theta = 55°$ except spectrum B. The peaks at 68 eV and 84 eV on spectrum A result from Al LMM transition and Al double ionization, respectively.[16] The AES spectrum at the analyzer angle $\theta = 10°$ for the clean surface is shown in Figure 5B. The peak due to Al bulk plasmon loss appears at 52 eV.[16] Because spectrum B was measured at small analyzer angle, the peak due to Al bulk plasmon loss in Figure 5B is enhanced compared with spectrum A. Figure 5C shows the AES spectrum at $\theta = 55°$ for the Al(111) surface, on which hydrogen of 1 ML was adsorbed at 110 K and its peak fitting by two Gauss-Lorentz line shapes. This spectrum indicates that a new AES transition takes place at 63 eV by the hydrogen adsorption at 110 K. Because the probability of interatomic AES transition between the Al surface and the adsorbed hydrogen is very low, this new transition is due to the AES transition between a new valence band, which the hydrogen adsorption at 110 K produces, and the inner shell of Al, that is to say, LVV transition. This peak due to Al LVV transition is expected to correspond to the state below 3 eV on the UP spectrum in Figure 4 (see below). The peak due to Al bulk

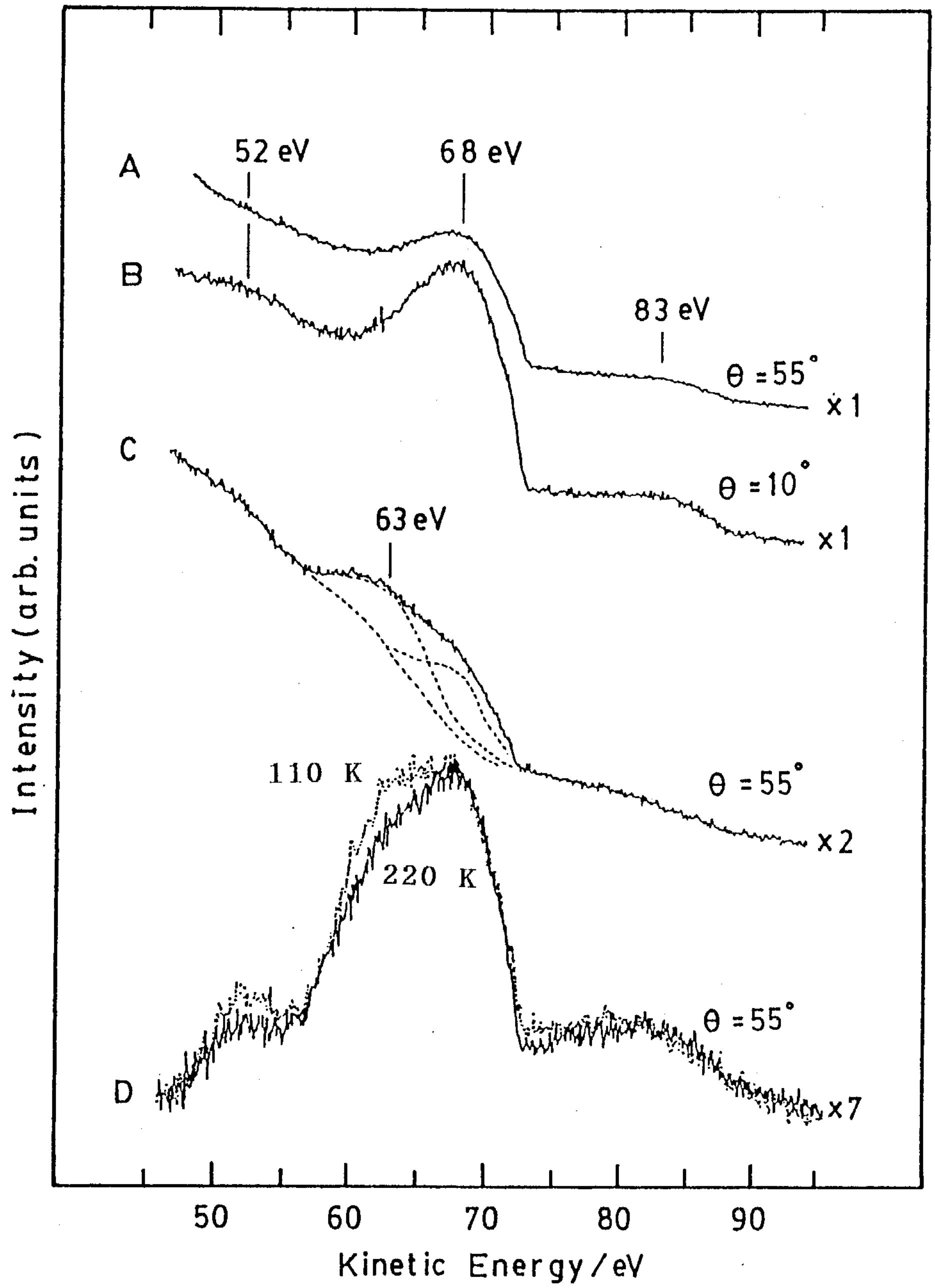

Figure 5. The AES spectra for the hydrogen adsorbed Al(111)surface.
A: Clean surface (θ = 55°).
B: Clean surface (θ = 10°).
C: The hydrogen of 1 ML adsorbed surface at 110 K.
D (solid line) : After the surface (1 ML, 110 K) was kept for 10 min at 220 K. Spectrum D was obtained after subtracting the background of secondary electron. A dotted line spectrum was obtained by subtracting the background from spectrum C.

plasmon loss at 52 eV in Figure 5C is enhanced compared with that of the clean surface (Figure 5A). This may concern that the state to have relation to Al bulk appears on the UP spectra in Figure 2. The AES spectrum for the surface measured at 100 K ~ 110 K after the surface in Figure 5C (1 ML H/Al(111)) was kept at 220 K for 10 min is shown as spectrum D (solid line). And, the spectrum D was obtained after subtracting the background of secondary electron from the measured AES spectrum. The dotted line shape is the AES spectrum after subtracting the back ground from spectrum C (110 K). It is recognized that the peak intensity at 63 eV become weak by the anneal at 220 K. Figure 6 displays the AES peak areas at 63 eV, which is LVV transition, as a function of the anneal temperatures where the 1 ML hydrogen adsorbed Al(111) surface was annealed for 10 min. The peak intensities at 63 eV decreases with increasing surface temperature. These results by UPS and AES measurements indicate that the electron in the valence band which is produced by hydrogen adsorption at 110 K is transferred to another electronic state with increasing surface temperature.

Recently, we investigated the hydrogen adsorbed Al(111) surface by means of high resolution electron energy loss spectroscopy (HREELS).[17] The vibrational modes (bending :~ 800 cm^{-1}, stretching : ~ 1600 cm^{-1}) for the terminal sites were observed at 85 K~ 110 K on the hydrogen adsorbed Al(111) surface. A new vibrational mode for the bridged sites of hydrogen (~ 1200 cm^{-1}) to add to these modes began to appear

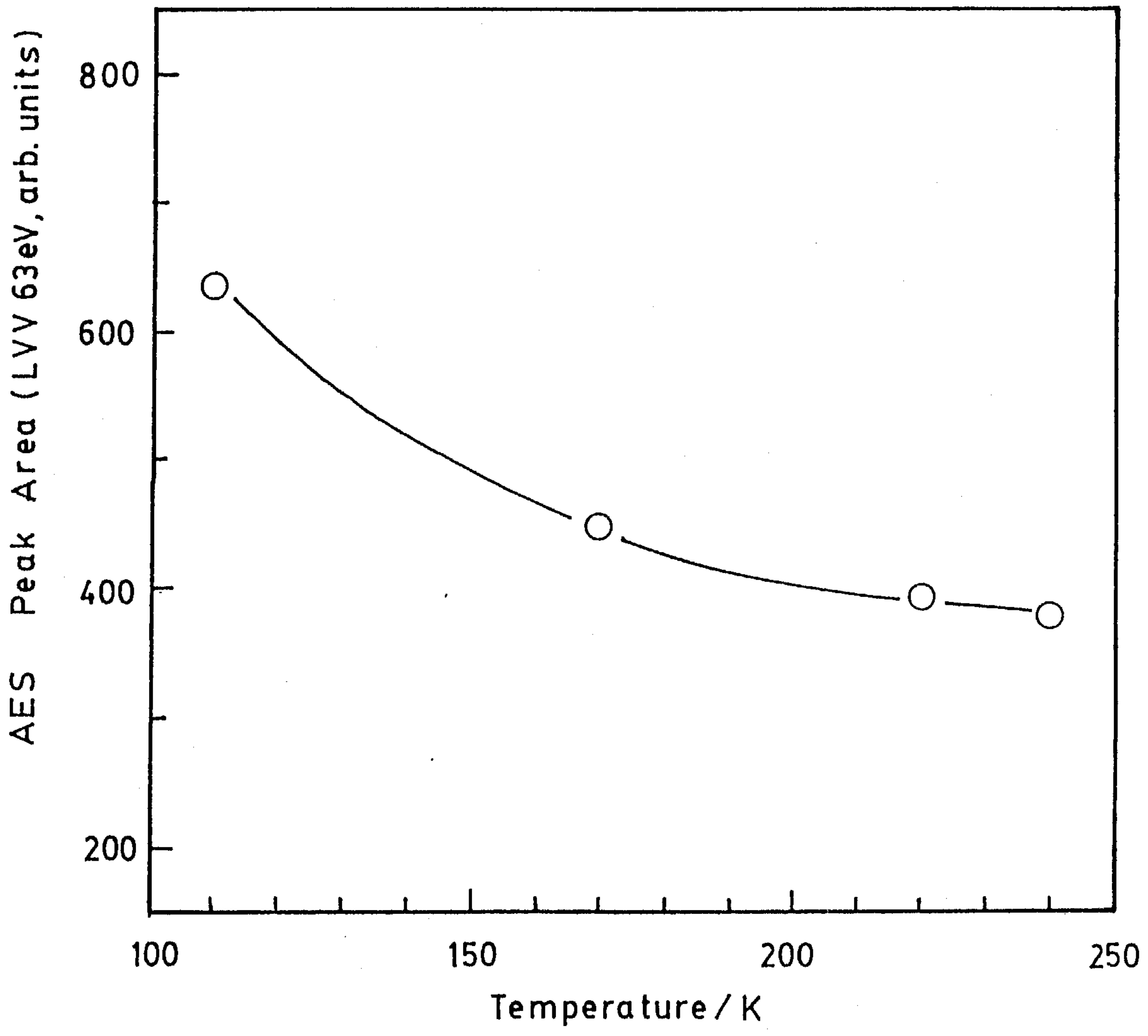

Figure 6. The peak areas for AES LVV transition (63 eV) as a function of anneal temperatures.

obviously at 150 K and grew up to ~ 240 K with increasing the temperature of the surface.[17] Consequently, these behaviors observed by means of UPS and AES would reflect the formation of the bridge site hydrogen with increasing surface temperature.

4-3. Adsorbed hydrogen atoms under the desorption of aluminum hydride.

The hydrogen adsorbed surface where aluminum hydride was desorbing was investigated. The change of the difference UP spectrum for the surface annealed at 280 K is shown in Figure 7. The hydrogen of 1 ML adsorbed Al(111) surface was heated to 280 K with heating rate of 2 K/s. Immediately after the surface was kept at 280 K fot the indicated time, the sample was cooled down to 100 K ~ 110 K and UP spectrum for the surface was measured at photoemission angle $\theta = 10°$. Although the desorption of aluminum hydride was observed at 300 K~ 350 K by TD experiments as shown in before section, aluminum hydride desorbs slowly at 280 K. Each spectrum in Figure 7 is normalized for comparison at the peak height of 5 eV. The intensity of the spectrum becomes weak by the gradual desorption of aluminum hydride with increasing anneal time. The line shape of the spectrum does not almost change until the anneal time of 540 s. However, above 660 s it is recognized that the peak at 7 eV decreases and the peak of 9.5

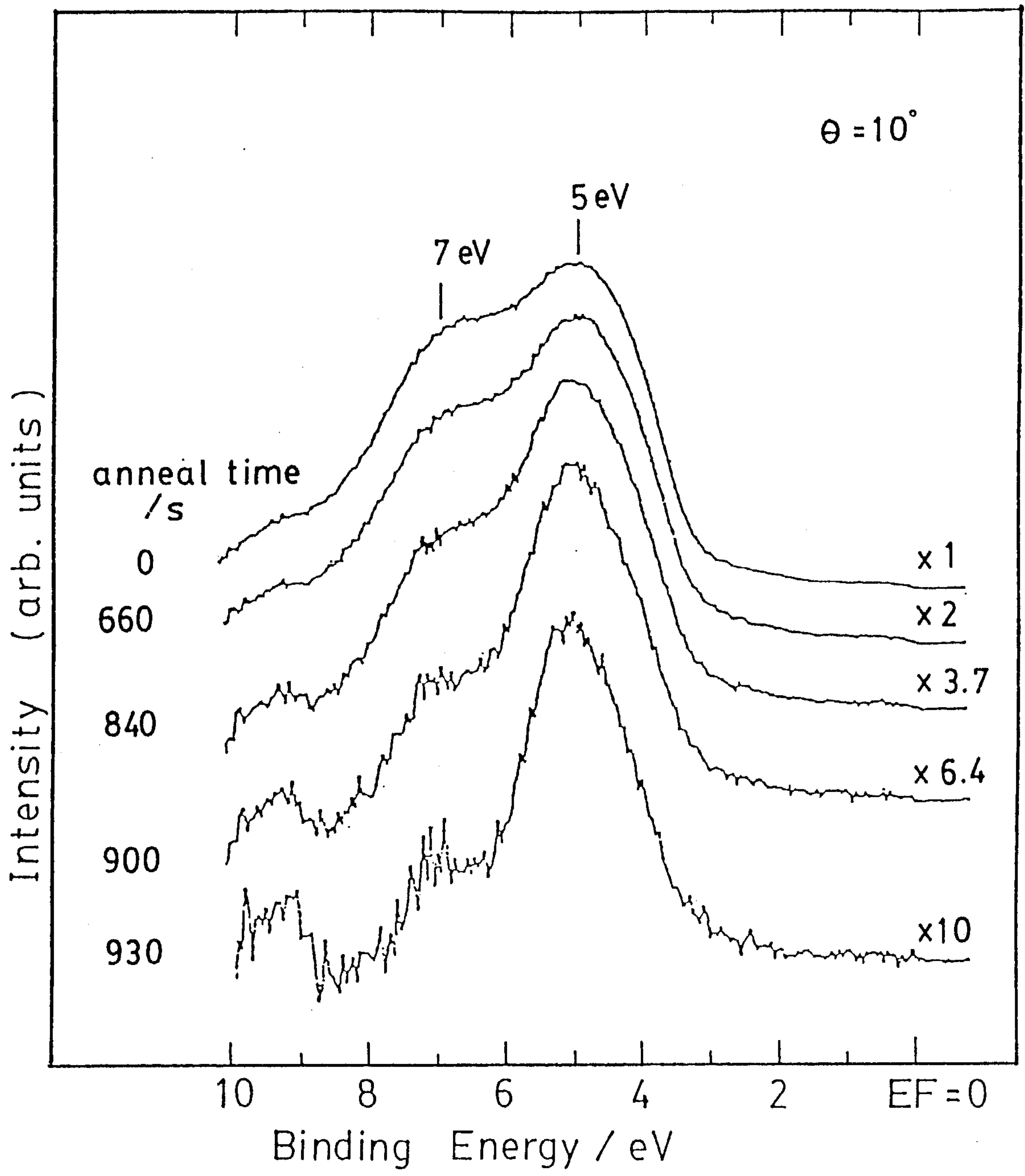

Figure 7. The difference UP spectra for the hydrogen of 1 ML adsorbed surface at 280 K. Each spectra were measured after the surface which was kept at 280 K for the indicated time was cooled down to 100 K ~ 110 K.

eV increases relatively to the peak of 5 eV with increasing anneal time. As a result, the line shape of spectrum at 0 s differs much from that at 930 s.

Figure 8 displays the peak areas of 5 eV and 7 eV divided by the Gauss-Lorentz line shapes in Figure 7 as a function of the anneal time. Comparing the total intensity (5 eV + 7 eV) with the peak intensity at 5 eV, it can be recognized that the ratio of the peak at 7 eV in total intensity begin to become small at 500 s~ 600 s. The anneal time dependence of FWHM for the peak at 5 eV in Figure 7 is shown in Figure 9. The FWHM decreases intensely above 500 s~ 600 s. These results suggest that a new state which is not observed below 280 K remarkably grows above the anneal time of 500 s~ 600 s at 280 K. This new state is expected to result from the precursor for the desorbed aluminum hydride. Because the line shape of the UP spectrum does not only depend on the amount of adsorbed hydrogen as mentioned in 4-1, the change of the spectrum in Figure 7 is due to both the remarkable formation of the precursor and the decrease of the hydrogen adatom by the desorption of aluminum hydride. Therefore, it is expected that aluminum hydride desorbs through the precursor which shows the spectrum of 930 s in Figure 7. Considering the peak at 7 eV as the state to concern the Al bulk as described in section 4-1, this precursor might have weak relation to the Al bulk compared with the adsorbed hydrogen atom at 110 K.

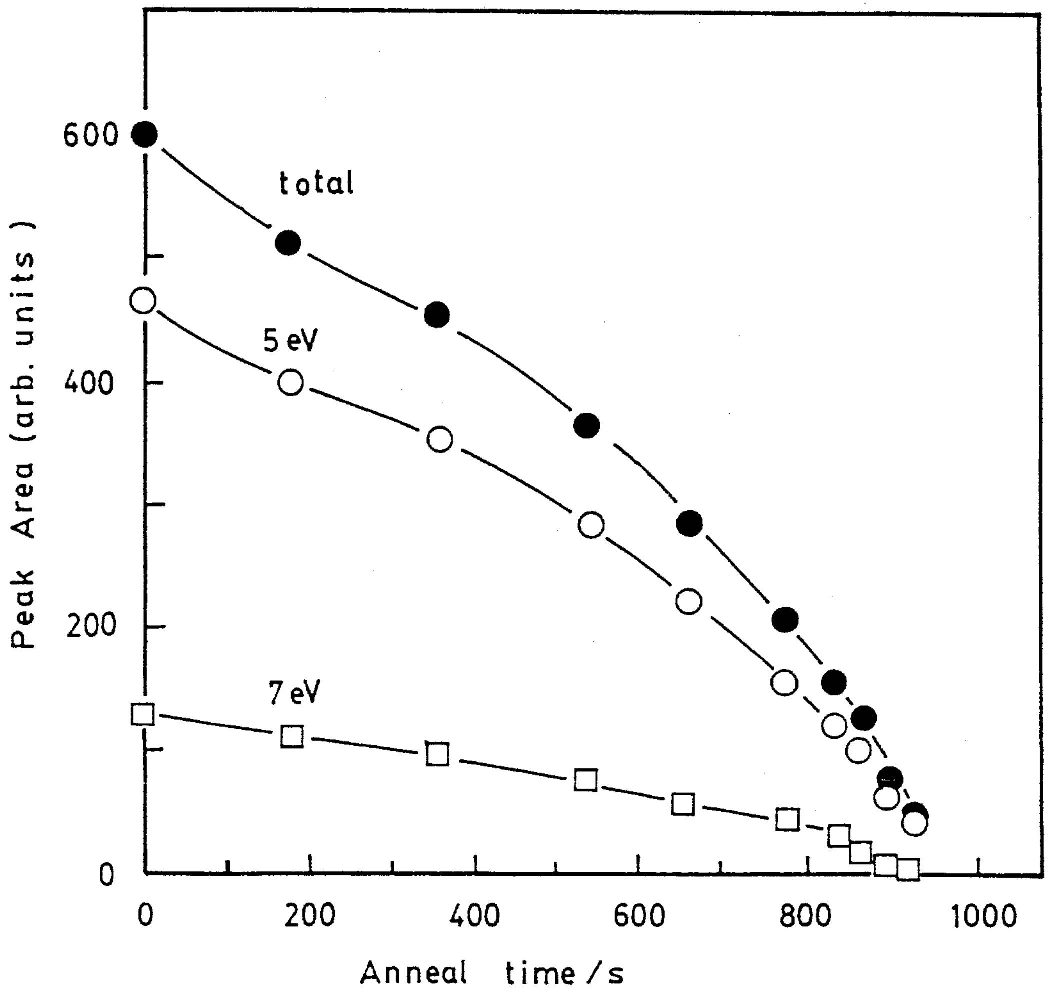

Figure 8. The peak areas at 5 eV and 7 eV in Figure 7 as a function of anneal times.

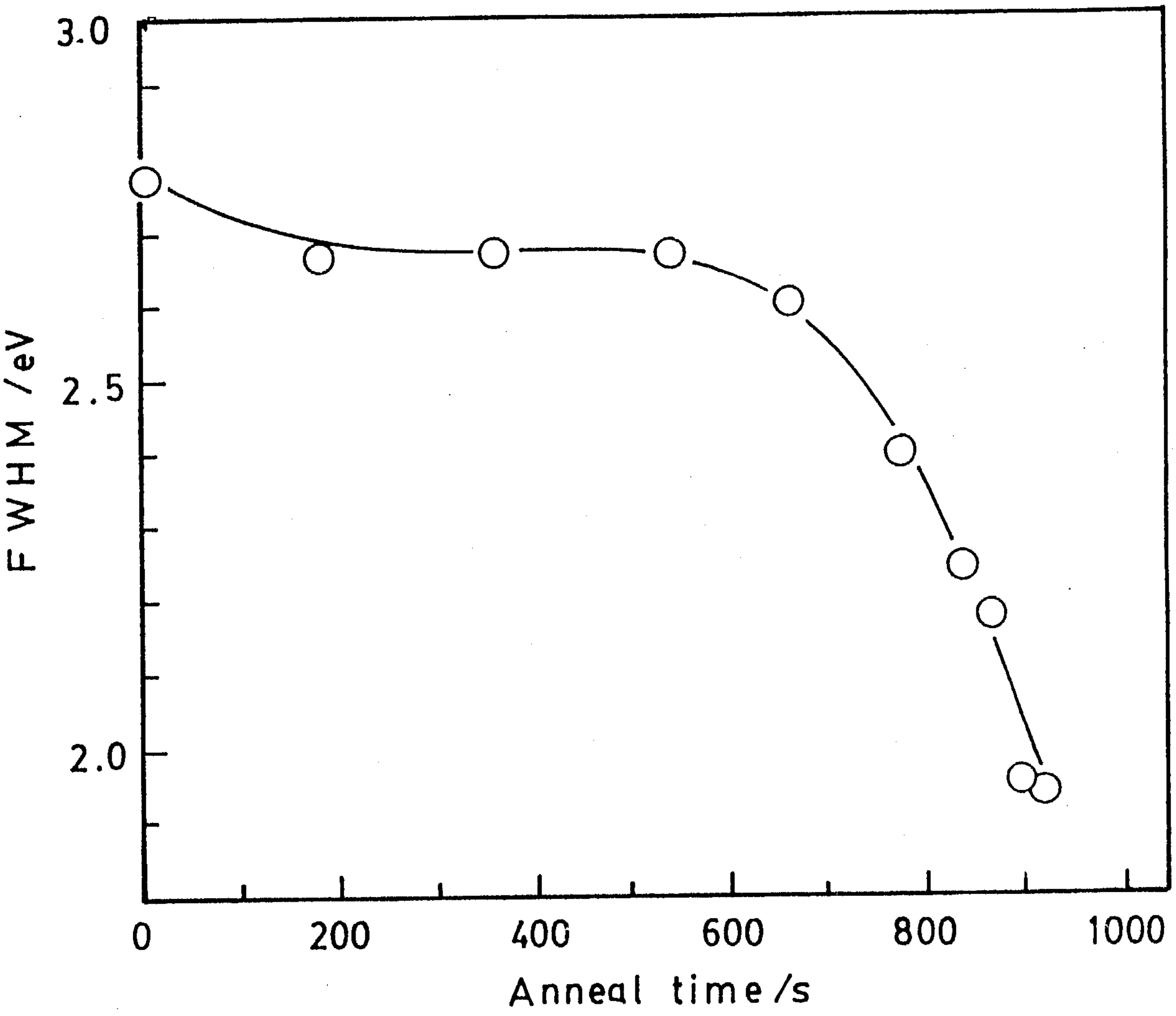

Figure 9. The FWHM of the peak at 5 eV in Figure 7 as a function of anneal times at 280 K.

5. Discussion

5-1. The electronic state of the hydrogen adsorbed Al(111) surface at 110 K

As shown in Figure 2, the states more than four on the hydrogen adsorbed Al(111) surface at the adsorption temperature (110 K) were observed by means of UPS. Because the state due to the Al 3s orbitals appears at 7 eV below the Fermi level on the clean surface, the states above 7 eV can be considered to result from the 3s orbital of Al. We estimated which of the atomic orbitals these states were due to with the help of the the first-principles calculations for the Al_{10} model cluster shown in Figure 1.

Figure 10 shows the UP spectrum for the Al(111) clean surface at θ = 10° and the eigen values for the orbitals of Al_{10} cluster. The total binding energy of this cluster is a -25.237 eV. For comparison, the most outer valence orbital in this cluster which lies in a 3.6 eV below vacuum level is identified with the Fermi level for the Al(111) clean surface whose work function ϕ is a 4.25 eV.[18] The length of the line at each eigen value means the number of electrons to occupy the orbital and show that two electrons occupy each orbital from 0.9 eV up to 8.4 eV. While electrons less than two occupy the orbitals below 0.9 eV since quasi-valence band is introduced into the calculation for this cluster. In Figure 10, three molecular orbitals of 5.5 eV, 6.4 eV and 8.4 eV are

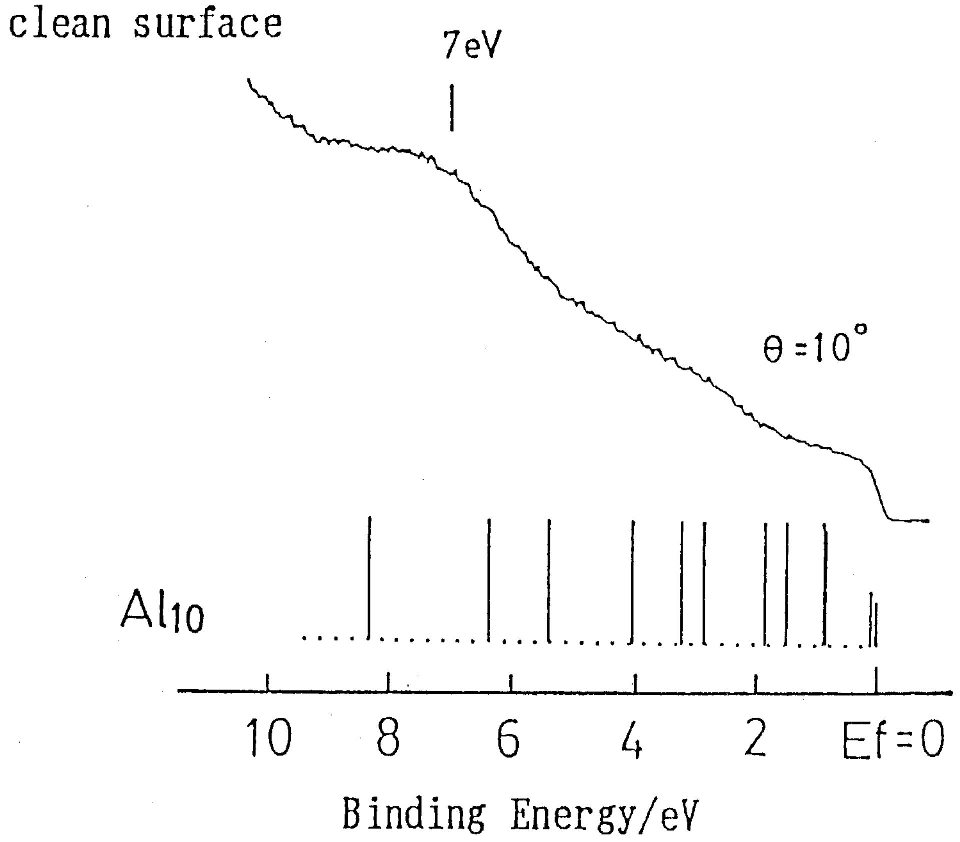

Figure 10. The UP spectrum for the clean Al(111) surface and the eigen values of the valence orbitals for the Al_{10} model cluster.
The eigen value for the most outer valence orbital is identified with the Fermi level for the clean surface.

due to Al 3s orbital and correspond to the peak at around 7 eV in the UP spectrum for the clean surface. The orbitals below 4.1 eV result from the valence orbitals of Al. From these results, the calculations for this Al cluster can be considered to reflect the Al(111) clean surface.

J.Paul using HREELS found experimental evidence of the formation of AlH_2 or AlH_3 at high surface concentrations of hydrogen on the Al(111) surface.[3] Our HREELS measurements also indicated that only the terminal sites of AlH_2 or AlH_3 existed on the hydrogen adsorbed Al(111) surface at 85 K ~ 110 K.[17] Taking account of these results, the hydrogen adsorbed Al_{10} clusters, in which two or three hydrogen atoms combined with a center Al atom in the first layer, were calculated. The geometries between the hydrogen atoms and the cluster were determined by the total binding energies for the clusters where total binding energies of the hydrogen adsorbed Al clusters became the largest.[8] Figure 11 displays the eigen values for molecular orbitals (MO) to concern Al-H bond strongly on the hydrogen adsorbed Al_{10} clusters and the geometries. Furthermore, the calculated result for the cluster which combines with a hydrogen atom and the difference UP spectrum for the hydrogen of 1 ML adsorbed Al(111) surface at 110 K (Figure 2C) are shown in Figure 11. The total binding energies of $Al_{10}H$, $Al_{10}H_2$ and $Al_{10}H_3$ clusters are -27.364 eV, -29.606 eV and -31.512 eV, respectively. In Figure 11, the MO which have negligible weak relation to Al-H bond are excepted by comparing the coefficients for the atomic orbitals of H

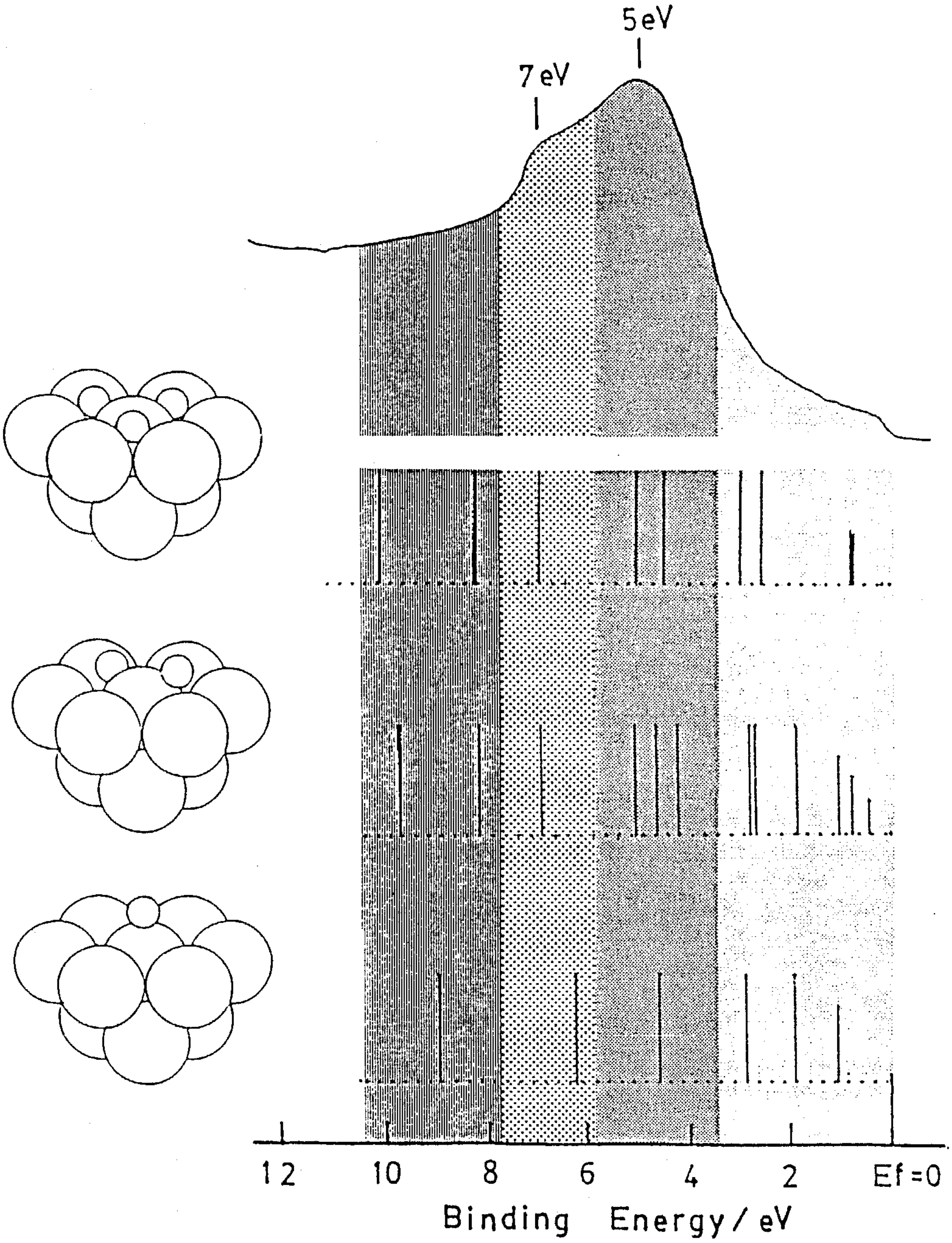

Figure 11. The difference UP spectrum for the hydrogen of 1 ML adsorbed surface at 110 K (Figure 2C) and the eigen values of the orbitals for $Al_{10}H$, $Al_{10}H_2$ and $Al_{10}H_3$ clusters.
The bond lengths for $Al_{10}H$, $Al_{10}H_2$ and $Al_{10}H_3$ are 0.1665, 0.1909 and 0.1765 nm, respectively.
The molecular orbitals to concern profoundly Al-H bond can be divided into four groups of ~ 3 eV, ~ 5 eV, ~ 7 eV and ~ 9 eV.

and Al. In Figure 11, the Fermi level of the difference UP spectrum is identified with the most outer valence orbitals in these clusters as Figure 10. The eigen values of the most outer valence orbitals below vacuum level in these clusters ($Al_{10}H$, $Al_{10}H_2$ and $Al_{10}H_3$) are almost equal to 3.6 eV. The difference UP spectrum is expected to reflect the relative relations among the eigen values of the orbitals which concern the Al-H bond strongly in these clusters.

As shown in Figure 11, many orbitals to have relation to the Al-H bond appear on the hydrogen adsorbed Al_{10} cluster. These orbitals can roughly be divided into four groups by comparing the coefficients of the atomic orbital functions for H 1s, Al 3s and Al 3p in these clusters. The first group at around 5 eV is due to the valence orbitals. These orbitals concern hydrogen most strongly among four groups and correspond to the local bonding state on Al-H bond. Considering the state of the local Al-H bonding to take place at ~ 5 eV below the Fermi level on many hydrogen adsorbed metal surfaces, the state at 5 eV on the difference UP spectrum in Figure 2 and 11 can be attributed to the orbitals in the first group. The state of the second group at 6.3 eV ~ 7.0 eV results from Al 3s orbital. The orbitals in this group are very expanded orbitals and more strongly attributed to the Al atoms in the second layer of the cluster than that of the first layer. In the calculations for $Al_{10}H_3$, the contribution from the Al 3s orbital at the first layer can be almost ignored. The state at 7 eV on the difference spectrum is considered to have relation to Al bulk by the photoemission angle dependence of the difference UP spectra shown in Figure 3. Thus, these results suggest that the peak at 7 eV below the Fermi level is not so much due to 3s orbital of the surface layer as that of the Al bulk. The orbitals in the third group, at which the contribution from Al 3s of the first layer is much larger than that of the second layer, appear at 8.2 eV ~ 10.2 eV. The binding energies of these Al 3s-like orbitals are higher than that of Al_{10} cluster shown in Figure 10 where the state due to Al 3s orbital appears at 5.5 eV ~ 8.4 eV. The energy level diagram of MO theory shows that the combination of two atomic orbitals leads to the formation of the more stable bonding MO. As a result, Al 3s-like orbitals at 8.2 eV ~ 10.2 eV in the hydrogen adsorbed Al clusters are attributed to the formation of bonding MO (σ orbital), which is more stable than the orbitals (~ 7 eV) due to Al 3s in Al_{10} cluster by the combination between H 1s and Al 3s. These orbitals would correspond to be the state at around 9 eV of the difference UP spectrum. As shown in Figure 11, each energy eigen values or characters for the orbitals which belong to these three groups (~ 5 eV, ~ 7 eV and ~ 9 eV) are almost identical at $Al_{10}H_2$ and $Al_{10}H_3$.

The orbitals below 3.2 eV which are due to valence orbitals (Al 3s + 3p) belong to the last group. Although the characters of each orbitals, especially the orbitals near the Fermi level are complex, the contribution from the Al atoms in the first layer of the cluster can be said to be somewhat larger than that in the second layer.

As shown in Figure 5, a new AES transition at the kinetic energy of 63 eV occurs when hydrogen was adsorbed on the Al(111) surface at 110 K. This new AES transition is expected to result from LVV transition. If localized or nonlocalized hole-hole interaction can be ignored in this AES transition, the energy of LVV transition (E(LVV) = 63 eV) due to the new valence band is simply expressed as follows[24,27]:

$$E(LVV) = E_{Al2p}(L) - 2E_{Al}(V)$$

where $E_{Al2p}(L)$ and $E_{Al}(V)$ are the binding energies below vacuum level of Al 2p core level and the new valence band on the hydrogen adsorbed Al(111) surface, respectively. As shown in section 4, our XPS measurements revealed the binding energy of Al 2p core level, where the hydrogen of 1 ML was adsorbed on the Al(111) surface at 110 K, to be almost equal to that of the clean surface (72.7 eV below the Fermi level). The work functions for the clean surface and the hydrogen of 1 ML adsorbed surface are 4.25 eV[18] and 4.25 eV + $\Delta\phi$ (=0.29 eV, our measurements) = 4.54 eV, respectively. From these values, the value of $E_{Al}(V)$ is about 7.1 eV (2.6 eV below the Fermi level). The valence band which is produced by the hydrogen adsorption to the Al(111) surface at 110 K is expected to appear at around 2.6 eV below the Fermi level. Thus, the state below 4 eV on the difference UP spectrum in Figure 11 can be considered to correspond to the valence band due to the hydrogen adsorption. The molecular orbitals at 2.5 eV~ 3.2 eV by the first-principles calculations for the hydrogen adsorbed Al_{10} clusters shown in Figure 11 would result from this valence band.

The assignment of the difference UP spectrum for the hydrogen adsorbed Al(111) surface at 110 K are summarized in Table 1.

These results reveal the characters for each states and the relations of eigen values among four states not to vary so much even if the number of hydrogen atoms of the terminal site on the Al cluster differ in each clusters. This means that the state due to the Al 3s of the second layer appears surely at 1.5 ~ 2.0 eV higher in binding energy than the local Al-H bonding state. If the calculations for these clusters reflect the hydrogen adsorbed Al(111) surface actually, we can say that the state at 5 eV is due to the local bonding state and the state at 7 eV result from the Al 3s of the bulk. And indeed, these calculated results are in good agreement with the result of our experiments. Except semiconductor surface such as Si, the UPS for hydrogen adsorbed non-transition metal (sp-metal) surfaces has not almost been measured. In the UP spectrum of the hydrogen adsorbed Si(111) surface, two states due to monohydride phase (Si-H) were observed at 9.8 eV and 12.0 eV below vacuum level, which are due to the local Si-H bonding state and Si 3s-like orbital, respectively.[13,21] These results differ from that of the Al(111) surface in the point

Table 1. The assignment of the difference UP spectrum for the hydrogen adsorbed Al(111) surface. At this temperature, there are only terminal sites.

states	Assignments
~ 4 eV	The Al valence band produced by the hydrogen adsorption.
~ 5 eV	The local bonding state of the Al-H bond.
~ 7 eV	The extended orbital due to the Al bulk 3s.
~ 9 eV	The orbitals due to surface Al 3s.

where the state due to the 3s-like orbital of bulk Al does not exist. As mentioned in the electronegativity, work function or jellium model of Al, Al surface is liable to discharge electron. On the other hand, the adsorbed hydrogen on the Al(111) surface has negative charge as shown in the work function change ($\Delta \phi = + 0.29$ eV). The negative hydrogen adatom is expected to attract the electron strongly from the Al surface liable to discharge electron. And indeed, the Mulliken population analysis for $Al_{10}H_2$ and $Al_{10}H_3$ clusters showed that a hydrogen atom on these clusters had the negative effective charge of -0.24 and -0.27, respectively. Therefore localizing electron in Al surface and bulk upon the adsorbed hydrogen might cause the peak at 7 eV, which is due to the extended orbital of the bulk Al 3s, on the UP spectrum for the hydrogen adsorbed Al(111) surface.

The formation of the terminal sites such as AlH_2 or AlH_3 at 85 K~ 110 K might reveal the mobility of hydrogen adatom at low temperatures to be enough high. On the Al(110) surface which reduces the mobility of hydrogen adatom, the desorption of aluminum hydride is remarkably disturbed and the hydrogen adsorption is entirely different from that on the Al(111) surface.[19,20]

5-2. The formation of the bridge site hydrogen.

Figure 4 and 5 suggest that the electronic state changes with increasing surface temperature. These behaviors can be expected to have relation to the formation of the bridged site hydrogen which has already been observed by HREELS measurements.[17] Unfortunately, we can not calculate the bridge site hydrogen on the Al cluster shown in Figure 1 because the cluster is too small for the calculations. In general, d-orbitals of surface metal atoms concern the formation of the bridged site hydrogen on transition metal surfaces. However, this can not explain the bridged site on the Al surface which is a sp-metal. The chemistry of electron-defficient compounds such as diborane (B_2H_4) and dialane (Al_2H_6) which have the bridging hydrogen may be available for understanding the bridged site on the Al surface. There is no spectroscopic result for Al_2H_6 as a free molecule because of the unstableness of Al_2H_6 molecule as mentioned before section. Therefore, we attempted to discuss this problem with help of the first-principles calculations for molecular AlH_3 and its dimer, Al_2H_6.

the eigen values of occupied orbitals and densities of states below vacuum level for AlH_3 and Al_2H_6 are shown in Figure 12. Each orbitals are occupied by two electrons. The eigen line width for an occupied orbital in Figure 12 is estimated at about 1 eV by the UP spectra for SiH_4 and GeH_4.[21] The states of 7.4 eV and 10.5 eV for AlH_3 in Figure 12 are due to Al 3p and Al 3s, respectively. Because there are two molecular orbitals at 7.4 eV and an orbital at 10.5 eV, the intensity ratio between the states of 7.4 and 10.5 eV is a 2 :

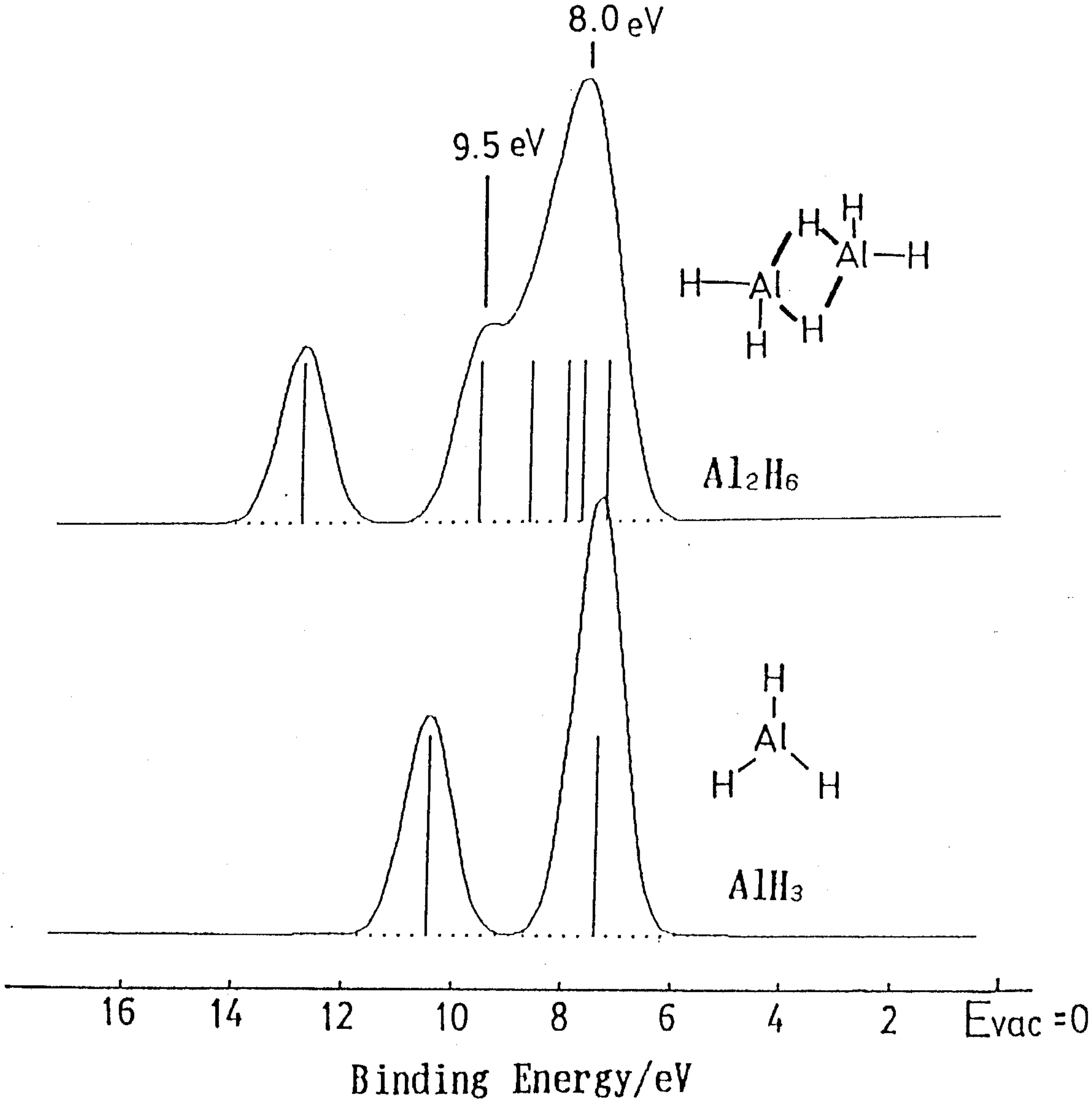

Figure 12. The eigen values and densities of states for the valence orbitals on AlH_3 and Al_2H_6 molecules.

1. This means that the bonding orbital of AlH_3 have the 3p-like character of 2/3 and the 3s-like character of 1/3, that is to say, sp^2 hybrid orbital. As shown in Figure 12, the valence orbitals of Al_2H_6 is somewhat complex compared with AlH_3. The molecular orbitals in Al_2H_6 can be analogized by the example of diborane (B_2H_6).[22] In electron deficient molecules such as diborane and dialane, two molecules which have sp^2 hybrid orbital as a monomer are easy to form its dimer through three-center two electrons bonding through two bridging hydrogen atoms. There are two sort of hybrid orbitals due to terminal metal-H bond and bridging hydrogen in these dimers.

The first-principles calculations revealed two states at 9.5 eV and 13.0 eV on Al_2H_6 in Figure 12 to result from Al 3s. These two statesdue to Al 3s are indicative of the existence of two hybrid orbitals in Al_2H_6. Furthermore, in Al_2H_6, several orbitals appear at around 8 eV. These orbitals are due to Al 3p and local bonding orbitals which concerns H 1s strongly. Comparing the calculations for Al_2H_6 with that of AlH_3 in Figure 12, the local bonding state and the states due to Al 3s are considered to change remarkably where bridging hydrogen is formed.

From these results, it is expected that the orbitals due to the bridging hydrogen on the Al surface appear at around the local bonding state and two states attributed to Al 3s where the bridged site is formed from the terminal site. As shown in Figure 4, the increases of the peak intensities at 5eV, 7eV and around 9 eV were recognized with increasing the temperature of the 1 ML hydrogen adsorbed Al(111) surface. The increased two states at 7 eV and 9 eV are due to Al 3s because there is the energy level of Al 3s more than 6 eV as shown in Figure 10. As a result, the change of this UP spectrum is likely to result from the formation of the bridging hydrogen. Indeed, considering the peak at 5 eV (9.5 eV below vacuum level) on the hydrogen adsorbed surface and the state at 8 eV in Al_2H_6 of Figure 12 to have same character as local bonding states, the increases (at 9.5, 11.5 and 13.5 eV below vacuum level) on the UP spectrum in Figure 4 are acknowledged to correspond mostly to the peaks (8.0, 9.8 and 13.0 eV)in the density of state for Al_2H_6 in Figure 12. While Figure 4 also reveals the electron in the state below 3 eV, which is new Al valence band produced by the hydrogen adsorption, to decrease with increasing surface temperature. Consequently, the states of the bridged site due to the local bonding orbital and the two kind of 3s orbital, to which the charge in the state below 3 eV is transferred on the formation of the bridged sites, are also expected to appear at 5 eV, 7 eV and around 9 eV, respectively. This suggests that the binding energy of the terminal site hydrogen on the Al(111) surface is almost equal to that of the bridging hydrogen because the terminal site also has the states at 5 eV, 7 eV and 9 eV. This is supported by the results which had already been reported.[23] Hjelmberg reported that hydrogen atom of the terminal and bridged site on Al(111) surface had almost same binding energy.[23] In the previous section, we concluded the state at around 7 eV on the

Al surface (110 K), which has the only hydrogen adatom of the terminal site, to result from the interaction between negative hydrogen adatom and bulk Al 3s. As a result, the state due to the bridging hydrogen add to the state attributed to the Al bulk 3s would appear simultaneously at around 7 eV below the Fermi level with forming the bridged site (see below).

Figure 4 shows the decrease of new valence band below 3 eV which occurs by hydrogen adsorption with the formation of the bridging hydrogen. The decrease of AES LVV transition, which is due to new valence band, shown in Figure 5 also supports this behavior. This suggests that the charge on the bridging hydrogen is more negative than that of the terminal hydrogen. A hydrogen atom of molecular AlH_3 was reported to have negative effective charge of -0.10.[24] The Mulliken population analysis for Al_2H_6 indicated that a bridging hydrogen atom of Al_2H_6 has the more negative effective charge of -0.13 compared with AlH_3.[8] Now, although we can not compare the charge of the terminal hydrogen with that of the bridging hydrogen on the hydrogen adsorbed Al(111) surface, we can say that the bridged site is more negative than the terminal site. Considering the Al surfaces to be liable to discharge electron as shown in the jellium model, one can recognize this tendency to increase on Al surfaces. This is supported by our calculations for the hydrogen adsorbed Al cluster. As mentioned before, the Mulliken population analysis for $Al_{10}H_2$ and $Al_{10}H_3$ shown in Figure 11 revealed that a hydrogen atom on these clusters is more negative than hydrogen atoms in molecular AlH_3 or Al_2H_6. The formation of the more negative bridged site may cause the decrease of the valence band which occurs by the hydrogen adsorption.

Although the detail structure of aluminum hydride in the solid phase is not yet elucidated, it is expected to be the structure as $(AlH_3)_n$ polymerized by the bridging hydrogen.[25] The bridging hydrogen is easy to occur in electron-defficient compounds whether it is molecular or solid. The change of electronic state with increasing the temperature of the Al surface reflect the formation of the bridging hydrogen due to the electron deficiency of aluminum hydride on the Al surface liable to discharge electron.

5-3. The desorption of aluminum hydride

The formation of the bridged site from the terminal site with increasing surface temperature is indicative of the coexistence of the terminal and bridged sites at 280 K, at which aluminum hydride begins to desorb. The vibrational modes for the terminal site and bridged site were observed at 280 K by HREELS measurements.[17] As the result, Both states due to the bulk Al 3s and the Al 3s of the bridging hydrogen can be expected to appear at around 7 eV in Figure 7 which displays the difference UP spectra at 280 K.

Figure 7 reveals the line shape change of the difference

UP spectrum where the intensity of the peak at 7 eV relatively decreases with increasing the anneal time at 280 K, at which aluminum hydride desorbs gradually. A HREELS experiment under the same condition in Figure 7 showed that the intensity ratios of each vibrational modes due to the terminal and bridged sites were constant even if the concentration of hydrogen atom decreased by the desorption of aluminum hydride.[17] This result shows that the decrease of the bridged site does not cause the decrease of the peak at 7 eV. Furthermore the line shape of the UP spectrum does not depend on the hydrogen concentration as mentioned before. Taking account of them, the change of the spectrum might be not merely due to the decrease of the surface hydrogen concentration but the increase of a new surface hydride which is the precursor for the desorbed aluminum hydride. Figure 8 shows that the intensity of the UP spectrum decrease rapidly above the anneal time of 500 s ~ 600 s and the line shape of the spectrum changes with the decrease of hydrogen adatom. These results also support the desorption of aluminum hydride through this surface hydride.

Therefore, the difference UP spectrum at 930 s in Figure 7 can be considered to show more closely the surface hydride formed at this temperature. Comparing this spectrum with the difference UP spectra for the hydrogen adsorbed Al(111) surface at 110 K, at which the only terminal sites are observed, we can say that the interaction between hydrogen adatom and the Al bulk on the precursor formed at 280 K become weaker than that at 110 K because the UP spectrum at 930 s in Figure 7 has a smaller peak at 7 eV than that at 110 K. This is the most likely to result from the formation of a molecular-like precursor under this condition. If the molecular-like precursor is formed on the surface, a hydrogen atom in the precursor would have weaker interaction with the bulk compared with an adsorbed hydrogen. The decrease of the FWHM shown in Figure 9 also supports the formation of the molecular-like precursor on the surface because molecule which has intermittent energy level is smaller in the peak width of the UP spectrum than surface of continuous energy level. Figure 13 displays the spectrum at 930 s in Figure 7 and the density of state for Al_2H_6 in Figure 12. The peak at 8 eV below vacuum level for Al_2H_6 is identified with the peak of 9.3 eV (5 eV below Fermi level) on the spectrum of 930 s in Figure 7 because these peaks have the same character which is local bonding state. One can recognize the line shape of the UP spectrum to resemble closely the density of state for Al_2H_6. Although a density of state is not equal to an UP spectrum in general, it reflects the line shape of the UP spectrum. Thus, this precursor formed on the surface may be molecular Al_2H_6-like. Electron deficient compounds such as BH_3 or AlH_3 are easy to become dimer by three-center bonding of the bridging hydrogen. And indeed, the formation of the bridged sites was observed in this system. From these results, it is enough possible that Al_2H_6 desorbs through the molecular Al_2H_6-like precursor. The interatomic distance on Al(111)

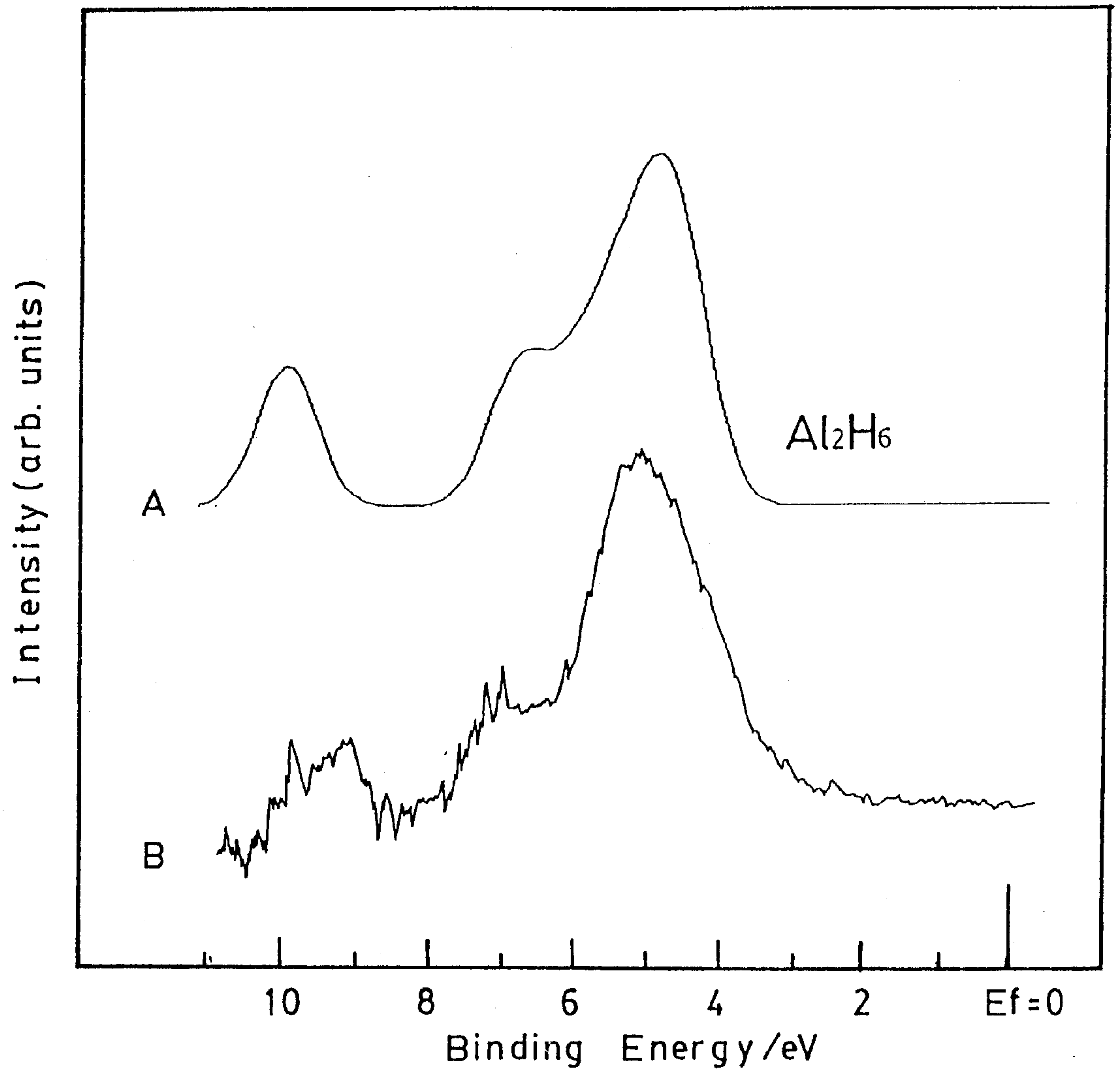

Figure 13. The difference UP spectrum at 930 s in Figure 7 and the density of state for the valence orbitals of molecular Al_2H_6.

surface is 0.2863 nm. This value is close to the distance (0.2602 nm) between two Al atoms in Al_2H_6 by the first-principles calculations (Figure 1).[7,8] The similarity between the geometries of Al(111) surface and Al_2H_6 might lead to the precursor of molecular Al_2H_6-like. As mentioned in section 4, the mass signal of AlH_3^+ (m/e=30) was detected in the desorbed species. This signal might not be due to desorbed AlH_3 but the mass fragment for desorbed Al_2H_6.

All of the results mentioned above indicates the charge transfer from Al to hydrogen atom. The localization of electron on the adsorbed hydrogen always has relation to whole process from the hydrogen adsorption to the desorption of aluminum hydride. As mentioned above, the calculations for the hydrogen adsorbed Al_{10} clusters are indicative of negative hydrogen atoms on the terminal sites. Furthermore, the hydrogen atom on the bridged site, which is formed with increasing surface temperature, is expected to have more negative charge than that of the terminal site. Localizing the electron in Al upon the adsorbed hydrogen can be considered as a kind of "oxidation" for Al. As a dry etching process for Al surfaces, the reaction between Cl_2 and Al surface has ever been used.[26] In this reaction, the "oxidation" by chlorine breaks Al-Al metallic bond in the surface and bulk and leads to the desorption of aluminum chloride such as $AlCl_3$ and Al_2Cl_6. Although the adsorbed hydrogen is not likely to break Al metallic bond directly, Localizing electron upon the adsorbed hydrogen might weaken Al-Al metallic bond and is expected to be a driving force to form the desorbed aluminum hydride. Furthermore, geometrically, Al(111) surface is considered to have surface structure liable to form the surface precursor of Al_2H_6-like. As a result, a kind of "oxidation" by the adsorbed hydrogen adatom on the Al surface liable to form molecular aluminum hydride might lead to the desorption of aluminum hydride.

The desorption of aluminum hydride from the hydrogen adsorbed Al(111) surface to be the simple-looking system is actually very complex. This complexity would result from several processes, which are the occurrence of the terminal sites, the formation of the bridging hydrogen and the molecular-like precursor, up to the desorption of aluminum hydride.

6. Conclusions

The formation and desorption of aluminum hydride on the hydrogen adsorbed Al(111) surface were studied by surface analytical techniques and calculations. Main results are concluded as follows:

1. Hydrogen atoms are adsorbed on the Al(111) surface as the terminal hydrogen such as AlH_2 or AlH_3 at 110 K. In the Al-H bond, the expanded orbital to concern with Al3s of the Al bulk occurs to add to local bonding orbital on the surface layer. A new valence band on the Al surface appears at around 2.5 eV by the hydrogen adsorption.

2. A part of the terminal hydrogen changes into the bridging hydrogen up to ~ 250 K increasing the temperatures of the surface. Because the more negative bridged site compared with the terminal site occurs, the valence band which is formed by the hydrogen adsorption decreases with the formation of the bridged sites.

3. At the desorption temperature (280 K~), aluminum hydride desorbs through the surface hydride which has weak relation to the Al bulk. This surface hydride may be the precursor of molecular Al_2H_6-like.

4. Localizing electron upon the adsorbed hydrogen is expected to be a driving force to form the desorbed aluminum hydride, Furthermore Al(111) surface is considered as the surface liable to form aluminum hydride.

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6. Etching of aluminum film by hydrogen atoms.

1. Introduction.

A demand for precise dry etching is increasing in the field of semiconductor industry, Very recently in the field of construction of micro-machines and so on.[1,2] Aluminum is rather extensively used as a material of electrodes and wirings of semiconductor devices. So far dry etching of aluminum has been performed by using halogen containing compounds as etchants. This dry etching process, however, has many substantial problems, for example impurities like carbon or halogen infect products or strict post treatments are needed to prevent pollution.

In the course of studies about surface chemistry of aluminum single crystal surfaces, we observed that aluminum hydride desorbed from a hydrogen adsorbed Al(111) surface as mentioned in section 4.[3,4] The mass spectroscopic studies suggested that only aluminum hydride such as Al_2H_6 or AlH_3 desorbed from the hydrogen adsorbed Al(111) surface. This result means the desorption of much aluminum hydride and the availability of this reaction as a dry etching process for Al surfaces. In this study, we estimated the efficiency of the reaction between adsorbed hydrogen and aluminum. Aluminum hydride can not permanently exist as a stable gas as mentioned in section 4 although the existence of Al_2H_6 and AlH_3 under vacuum has been confirmed. For this reason, TD experiments by means of mass spectrometer can not quantify the desorbed aluminum hydride. However, investigating the decresed amount of surface Al atom may lead to the estimation for the amount of desorbed aluminum hydride. Based on this conception, the experiments for a hydrogen adsorbed Al film deposited on a Mo(111) surface were carried out. The amount of surface Al atom removed by the desorption of aluminum hydride can be estimated by the AES measurements for Al and Mo on this surface. Through these experiments, it was demonstrated that about 1/3 of Al atoms in the surface Al atoms desorbed as aluminum hydride from the hydrogen of saturated coverage adsorbed Al surface. This result indicates that the etching efficiency of Al film by hydrogen atoms is high and hydrogen atoms is a good etchant for aluminum which meets the present demand.

2. Experimental.

The experiments were performed in the UHV chamber B. A disk shaped Mo(111) single crystal (ca. 3.5 mmφ x 1.5 mm) was used as a substrate. Because deposited Al atoms are liable to diffuse into the metal bulks of transition metals to have low melting points, whose melting points,[5], the Mo surface to have the high melting point (2883 K) was selected as the substrate. The Mo surface was polished as the polishing of the Al(111) surface mentioned in section 2. it was fastened to a manipulator by a similar to method which was mentioned previously for a Al(111) single crystal (section 2). The cleaning of the Mo(111) surface was performed by the cycles of Ar^+ bombardment at room temperature and annealing at 1073 K. The deposition of Al onto the Mo(111) surface was reproducibly controlled by resistively heating a 0.5 mm diameter Ta wire around which an Al wire (99.999 %) was wrapped. This evaporation source was covered with a shield can to collimate aluminum evapolation toward the substrate and to prevent a spurious effect of outgassing. Aluminum was deposited on the substrate which was held at 473 K. The deposition process was monitored by intermittently rotating the substrate toward the analyzer and measuring Auger spectra for Al LMM (68 eV) and Mo MNN (186 eV). AES measurements were performed by Al $K\alpha$ line ($h\nu$ = 1486.6 eV). Aluminum deposits on a Mo(111) surface in a layer by layer fashion.[6]

3. Results and Discussion.

Figure 1 shows AES peak-to-peak intensities of Al LMM and Mo MNN as a function of deposition time. With the progression of the deposition, the AES peaks for Al LMM increased and that for Mo MNN decreased in intensity. Two distinct changes in slopes for Al LMM and Mo MNN could be seen at 7.5 min. and 13.5 min. of deposition time. So we could clearly identify the completion of the first Al layer and the second Al layer. Values of AES peak-to-peak ratio, Al LMM (68 eV)/ Mo MNN (186 eV), for the first Al layer (deposition time 7.5 min.)

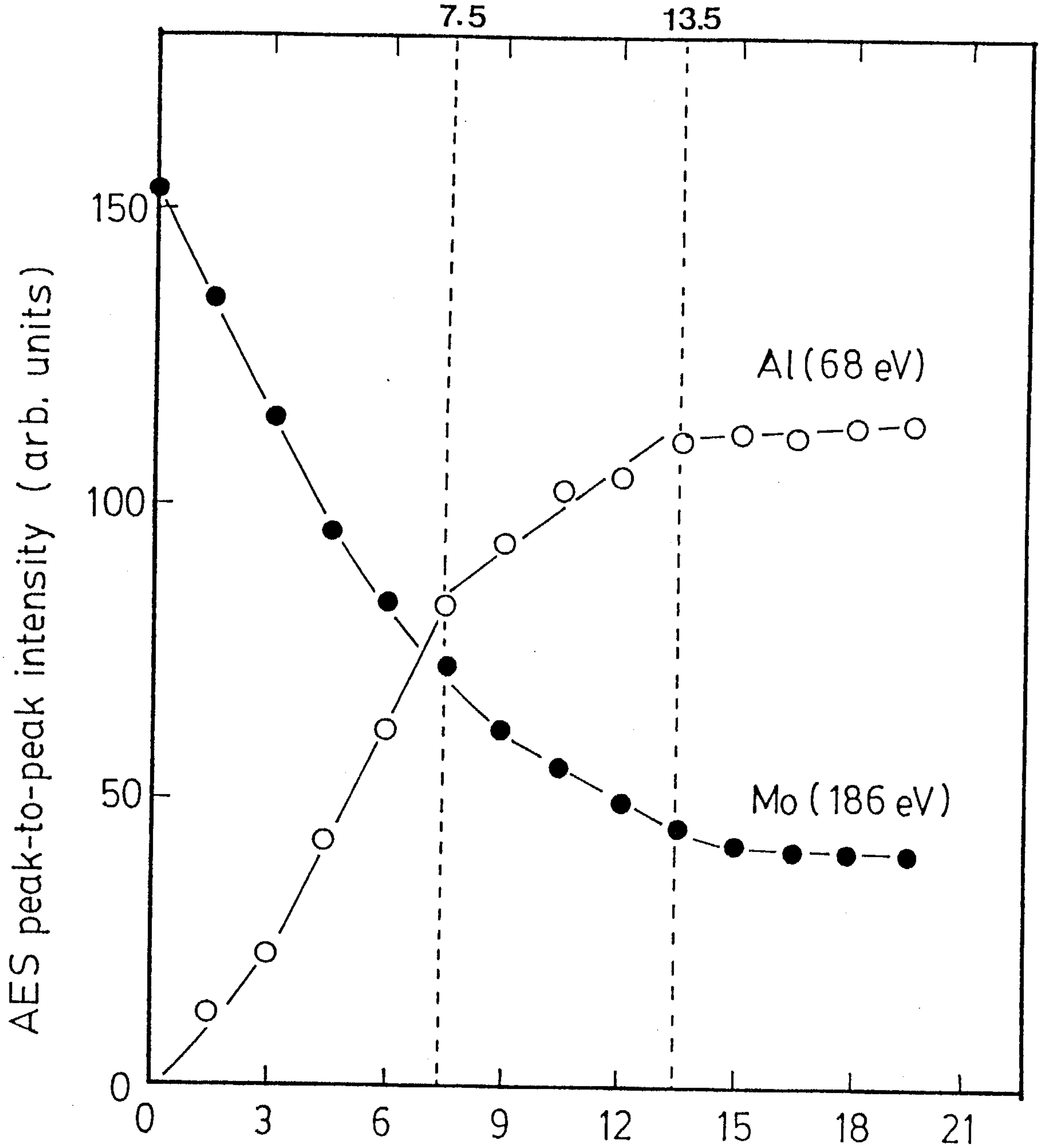

Figure 1. AES intensities of Al LMM (68 eV) and Mo MNN (186 eV) as a function of deposition time for Al on Mo(111).

and the second Al layer (13.5 min.) are 1.2 and 2.7, respectively. For a Al/Mo(111) layer, the AES intensity of the Mo (186 eV) is simply expressed as follows:

$$I = I^{\circ} \, EXP(-d/\lambda)$$

where I° is the intensity of Mo (186 eV) for pure Mo metal, d is an average thickness of Al overlayer and λ , which is the escape depth of Auger electrons for Mo(186 eV) in Al, is 0.47 nm, respectively.[7] From the above equation, we estimated the thickness of Al overlayer after the completion of second layer to be 0.61 nm. Since the atomic diameter of Al is 0.29 nm, one atomic layer by one atomic layer deposition of aluminum was verified till the completion of the second layer. Figure 1 shows that intensities of Mo MNN is almost constant above 15 min. This strongly suggests that after the completion of second layer nuclear growth of Al began. Thus the growth of Al on Mo(111) is the Stranski-Krastanov mode under this condition of deposition.[8,9] In the whole experiments, Al film of 2 monolayer (ML) on the Mo(111), which was deposited at the deposition rate of 0.12 Al layer/min, was used. The AES intensities of Al and Mo on the surface were not changed by the annealing more than 2 hours at 473 K. This means that the deposited Al atom does not diffuse into the Mo bulk below 473 K.

The Al film was cooled down to indicated temperatures prior to exposure to hydrogen atoms. Hydrogen atoms were generated by thermal dissociation of ambient H_2 (99.99999 %, 5 x 10^{-7} mbar) with a heated tungsten filament at ca. 2000 K. The filament was set at the distance of about 5 mm above the surface. The time of exposure of hydrogen atoms to the Al film was controlled by changing the heating time of the filament. After exposing to hydrogen atoms, thermal desorption (TD) and AES were measured. Desorbed species were detected by a quadrupole mass spectrometer.

Figure 2 shows TD spectra of AlH_3^+ (m/e=30) and Al^+ (m/e=27) from the Al film, on which hydrogen atoms were adsorbed to 1 ML at 220 K. We defined the saturated amount of adsorbed hydrogen as 1 ML (section 3).[3,4] The saturated amount of hydrogen was reached with exposure time of 6 min under the condition mentioned above. TD experiments were carried out from 220 K to 470 K with a heating rate of 5 K/s. TD peaks of AlH_3^+ and Al^+ were detected at ca. 370 K. The shapes of these TD peaks were similar to that for a hydrogen adsorbed Al(111) surface.[3] This result indicates that aluminum hydride desorbs in the same way from 2 ML Al film on Mo(111) as from an Al(111) surface. TD peak of Al^+ in Figure 2 is resulted from the mass fragmentation of aluminum hydride.[3]

The desorbed amount of aluminum was quantitatively determined by measuring the decrease of the AES peak-to-peak ratio of Al LMM (68 eV) and Mo MNN (186 eV) before and after a TD experiment. It was confirmed that the AES peak-to-peak ratio Al(68 eV)/ Mo(186 eV) decreased from 2.7 (Al layer of 2 ML) to 2.2 after a TD experiment shown in Figure 2.

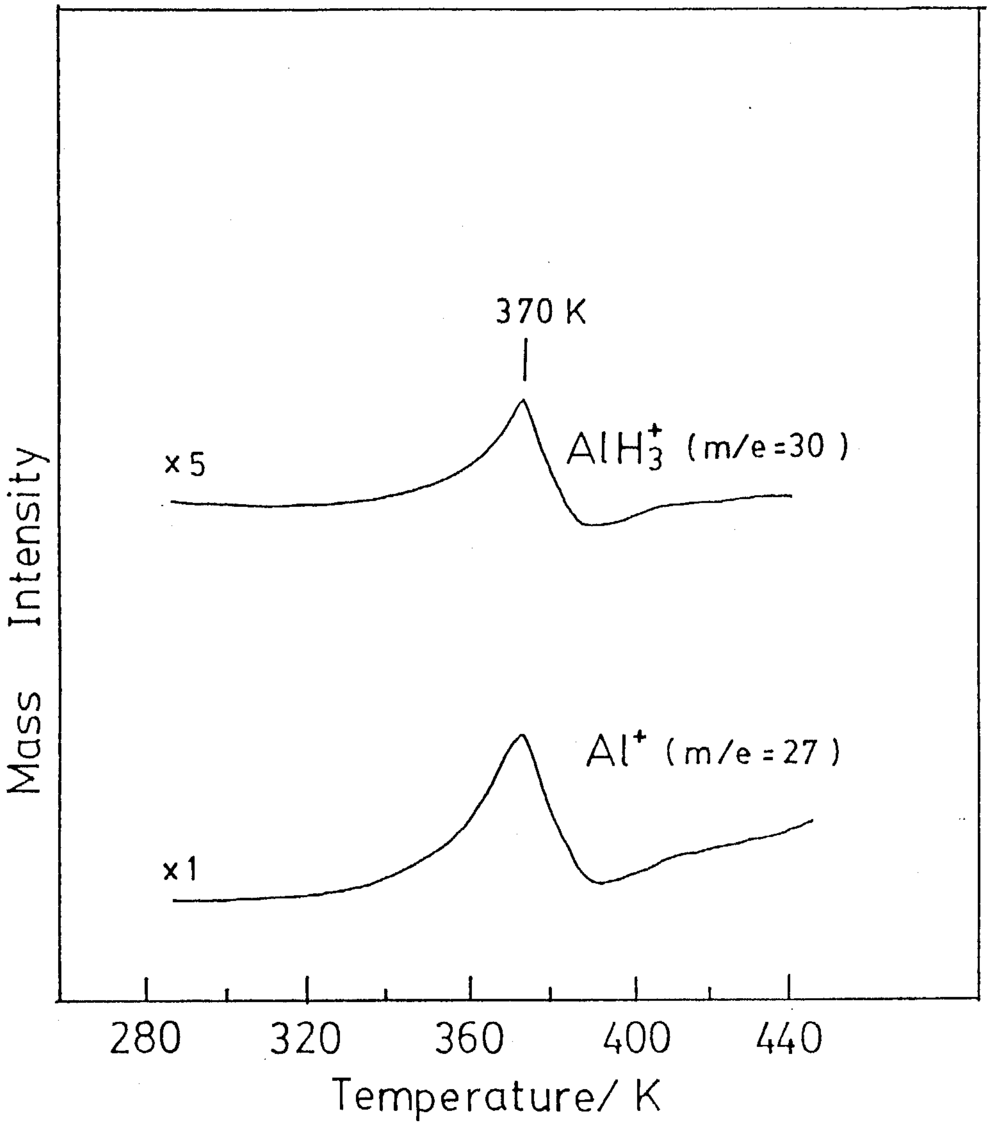

Figure 2. TD spectra of m/e=30 (AlH_3^+) and m/e=27 (Al^+) for 2 ML Al film which adsorbed 1 ML hydrogen atoms at 220 K.

This amount of decrease corresponds to about 1/3 layer of the second Al layer. From this experiment, we determined that about 1/3 ML of aluminum was desorbed from the 2 ML Al film, on which hydrogen adsorbed to 1 ML. As a result, the efficiency of the reaction between adsorbed hydrogen and surface aluminum is thus very high.

This result suggests that surface Al atoms may be etched continuously by exposing the thin Al film to hydrogen atoms above the temperature, at which aluminum hydride begin to desorb. To verify this idea, removal of Al atoms from the Al film was measured by exposing the film to hydrogen atoms at 410 K. The condition to generate hydrogen atoms with a hot tungsten filament was the same as mentioned above. AES was intermittently measured at 410 K by rotation the substrate to the analyzer. The result is shown in Figure 3. The left vertical axis indicates the ratio for AES peak intensities of Al(68 eV) and Mo(186 eV), the right vertical axis is layers of Al on this Al film deposited on Mo(111). The horizontal axis is the exposure time to hydrogen atoms. Figure 3 shows that all of the second Al layer was removed for about 20 min. For this exposure time, total number of hydrogen atoms which impinged on the film corresponded to 3.3 ML of the Al film. Thus all the hydrogen atoms reacted with the surface aluminum atoms and desorbed as aluminum hydride. By increasing the ambient pressure of H_2 to 1×10^{-6} and the filament temperature to ca. 2500 K, it was confirmed that the second Al layer etched within 5 min.

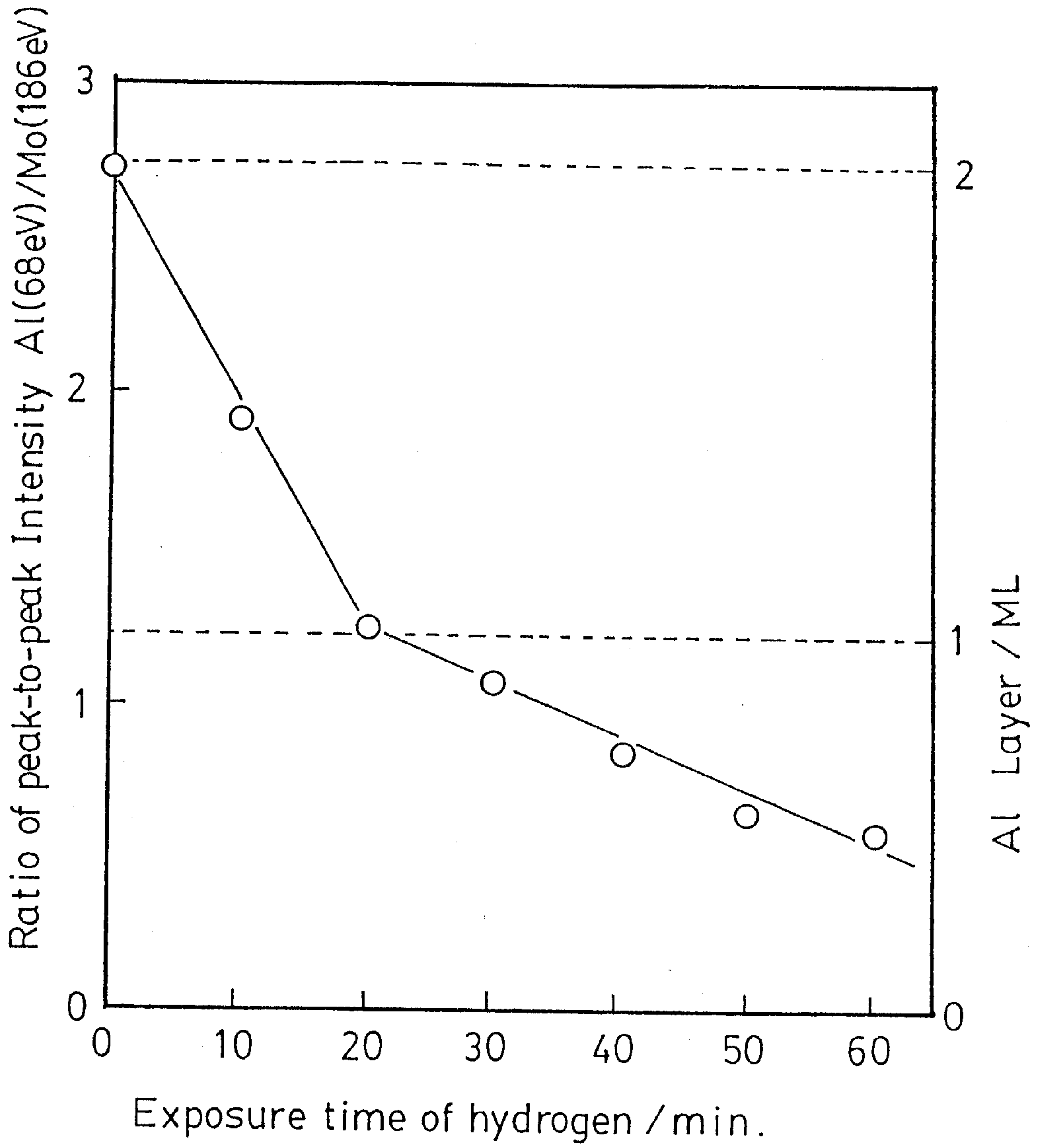

Figure 3. Decrease of the quantity of the Al film on the Mo(111) substrate which the Al film was continuously exposed to hydrogen atoms at 410 K.

It is interesting to note that the desorption rate of Al atoms for the first layer decreased compared with that of second Al layer. Because Al atoms of first layer contact with Mo atoms, it is expected that the reactivity of aluminum atoms and adsorbed hydrogen is different from the aluminum atoms on a aluminum substrate. Thus, desorption rate of Al atoms of the first Al layer may be smaller than that of the second layer.

These results indicate that the etching efficiency of Al is very high. It is rather easy to enhance the concentration of hydrogen atoms by using a radical beam source or a conventional plasma etching device. Thus hydrogen atoms are a potentially excellent selective etchant of Al films.

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7. Summary.

The reactions between hydrogen or CH_2I_2 and Al surface lead to the desorptions of aluminum compounds from the surfaces. As mentioned above, the dry corrosion by oxidation caused the formations and desorptions of aluminum compounds on the CH_2I_2 adsorbed Al(111) surface. On the hydrogen adsorbed Al(111) surface, even the desorption of aluminum hydride from the surface, which is a simple-looking system, takes place through several processes. The formation and desorption of metal compound by the reaction between an adsorbate and a metal surface have to occur through breaking the metallic bond in the surface and near surface.

Methyl halides react directly upon the transition metal surfaces such as Pt and Ni.[1,2] Although surface methyl group and surface halogen are produced by the reaction, organo-metal compound to have methyl group does not desorb but the desorptions of hydrocarbons such as C_2H_6 and CH_4 occur on these transition metal surfaces. The desorption of metal hydride from hydrogen adsorbed transition metal surfaces has never reported yet. Therefore the desorptions of organoaluminum compound and aluminum hydride from Al surface shows the characteristics of Al as non-transition metal.

Through the reaction of CH_2I_2 or hydrogen atom with the Al(111) surface, I would like to summarize the important factors for the formations and desorptions of aluminum compounds and mention the characteristic of Al which is different from transition metal.

Charge transfer from Al surface to adsorbate.

The charge transfer from Al to adsorbate always has relation to the reactions on the CH_2I_2 or hydrogen adsorbed Al surfaces. As mentioned in section 3, surface iodine or anionic methyl group produced by the decomposition of CH_2I_2 is expected to cause the dry corrosion at low temperature, in other wards, the decomposition of Al-Al metallic bond by the oxidation. On the hydrogen adsorbed Al(111) surface, hydrogen adatom at the adsorption temperature is considered to have negative charge from the results of the work function change ($\Delta\phi = +0.29$), UPS measurements and the first-principles calculations. Furthermore, the more negative bridging hydrogen is produced with increasing surface temperature.

Al as an element is positive as shown in the comparatively small electronegativity (1.47). Al surface is liable to discharge electron because work function reflects electronegativity. As a result, electron in Al surface and bulk near surface is liable to be localized upon negative adsorbates. This localization of electron would mean that adsorbates attract electrons in Al-Al metallic bond and weaken the metallic bond. The formation of alumina layer by oxygen and aluminum chloride layer by the reaction between Al surfaces and Cl_2 as a dry etching process at low temperatures show that strong oxidants are quite easy to break Al-Al metallic bond. On the CH_2I_2 adsorbed Al(111) surface, the dry corrosion at low temperature might be result from the formation of surface iodine or anionic methyl group which are electron attractive group. While, on the hydrogen adsorbed Al(111) surface at the adsorption temperature, the metallic bond in the Al surface is expected not to be broken as shown in the sharp (1 x 1) LEED spots. However electron is localized upon hydrogen adatom as shown in the UP spectra and the first-principles calculations for the hydrogen adsorbed Al_{10}.

Although the charge transfer from the Al surface to adsorbates might not directly lead to the formations of desorbed aluminum compounds, localizing electron upon negative adsorbates on Al surface liable to discharge electron might weaken the Al-Al metallic bond and cause the formations of desorbed aluminum compounds.

Surface structure.

On the CH_2I_2 adsorbed Al surface, the strong oxidation by CH_2I_2 would lead to the formations and desorptions of organic and inorganic aluminum compounds. However, only the localization of electron by adsorbed hydrogen might not break Al metallic bond and form molecular aluminum hydride because hydrogen can not strongly localize electron as iodine or methyl group. As mentioned in section 5, the formation of molecular Al_2H_6-like precursor is expected on the hydrogen adsorbed Al(111) surface. The distance between Al atoms in

Al_2H_6 is close to the interatomic distance on the Al(111) surface. As a result, the surface structure is likely to concern the formation of aluminum hydride.

On a hydrogen adsorbed Al(110) surface, which is uneven surface compared with the close packed (111) surface, the formation of aluminum hydride is remarkably inhibited. In result, both aluminum hydride and hydrogen desorb at each different temperatures. The amount of desorbed aluminum hydride from the Al(110) surface was less than 1/10 on the H/Al(111).[3,4] HREELS measurements for the H/Al(110) showed that the surface hydride formed on the Al(110) was completely different from the surface hydride on the Al(111).[4] These results are indicative of the surface structure sensitivity for the formation of aluminum hydride. This structure sensitivity might result from surface feature and Al density. The HREELS results that the terminal site such as AlH_3 or AlH_2 is formed on the Al(111) surface at low temperature are indicative of the enough high mobility of hydrogen adatom on the Al(111) surface.[4,5] The mobility of hydrogen adatom on the uneven Al(110) surface is expected to be lower than that of the close packed Al(111) surface. If the (110) surface decreases the mobility of the adsorbed hydrogen adatom, the formation of the desorbed aluminum hydride would be inhibited on Al(110) surface because the terminal sites such as AlH_3 or AlH_2 are hard to be formed compared with Al(111) surface. In addition, if aluminum hydride desorbs from the Al(110) surface through the molecular Al_2H_6-like precursor as the hydrogen adsorbed Al(111) surface, the probability to form this precursor on the (110) surface might be lower than that on the (111) surface. As a result, the formation and desorption of aluminum hydride on Al surfaces is likely to depend on the surface structure liable to form the aluminum hydride.

On the reactions between CH_2I_2 or hydrogen and the Al(111) surface, it is expected that the charge transfer from the Al surface to adsorbates is the most important factor for the formations and desorptions of aluminum compounds on the surface. Furthermore, on the hydrogen adsorbed Al surface, the surface structure to add to charge transfer might be important for the formation of aluminum hydride.

Aluminum surface as non-transition metal.

As mentioned above, if hydrocarbon halides react on transition metal surfaces, organometallic compound which has metal-carbon σ bond does not desorb but hydrocarbons desorb. Many of organo transition metal complex which have metal-carbon σ bond are unstable and can not exist as stable compound without stabilizing ligand such as cyclopentadienyl or carbon monoxide.[6] For example, although $Ti(CH_3)_4$ is decomposed at around 220 K, $Ti(CH_3)_4$(bipy) is stable and is not decomposed to ca. 273 K. Therefore the desorbed organoaluminum compound, which has stable $Al-CH_3$ bond, from the CH_2I_2 adsorbed Al(111) surface displays the characteristic as non-transition metal of Al in organo metallic chemistry.

Up to date, the desorption of metal hydride from hydrogen adsorbed transition metal surfaces has never been observed. After this, it will not be observed. Many of adsorbed hydrogen adatoms on transition metal surfaces are charged with negative charge. Unfortunately, we can not compare the charge of hydrogen adatom on the Al(111) surface with that on transition metal surfaces because the systematic study of the effective charge for the hydrogen adatom on metal surfaces has never been performed. Although electron is localized upon the adsorbed hydrogen on transition metal surfaces, transition metal hydride would not desorb because the metallic bond of transition metal is very strong compared with that of Al as shown in the high melting points and pure transition metal hydride as a free molecule is hard to be formed.

Through the phenomena on the CH_2I_2 or hydrogen adsorbed Al(111) surface, the characters of Al as a non-transition element and the chemical characters of Al such as the formation of electron defficient compound can be recognized to appear on the surface reactions, too. Actually, these surface reactions are very comlex and depend on many factors such as surface structure and so on.

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