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著者	岩本 光正, 田口 大
Authors	Mitsumasa Iwamoto, Dai Taguchi
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Research Trend in Thermally Stimulated Current Method for Development of Materials and Devices in Japan

Mitsumasa Iwamoto and Dai Taguchi

Department of Electrical and Electronic Engineering, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

ABSTRACT

Thermally stimulated current (TSC) measurement is widely used in a variety of research fields, i.e., physics, electronics, electrical engineering, chemistry, ceramics, biology, etc. TSC is short circuit current and it flows due to displacement of charges in samples during heating. The TSC measurement is very simple, but TSC curves give much important information on charge behaviors. In 1970's, TSC measurement made a great contribution to the development of electrical insulation engineering, to the development of semiconductor device technology, and so forth. Accordingly, TSC experimental technique and its analytical method had advanced. On the other hand, during the past several ten years, many new molecules and advanced functional materials have been discovered and developed. Along with this situation, TSC measurement has attracted much attention in industries and in academic laboratories as a way for characterizing discovered new materials and devices. This review reports the latest research trend in TSC method for development of Materials and Devices in Japan.

1. Introduction

Thermally stimulated current (TSC) measurement is widely used in a variety of research fields, i.e., physics, electronics, electrical engineering, chemistry, ceramics, biology, etc. TSC is short circuit current and it flows during heating due to displacement of positive and negative charges (electrons, holes, ions, etc.) as well as rotational motion of permanent dipoles in samples, due to phase transition of materials, and so forth. The electrical circuit used for the TSC measurement is very simple and merely one electro-ammeter is installed, but recorded TSC curves give important information on charge behaviors. This fact motivates us to employ TSC measurement as an important way for characterizing materials and devices. In 1970's, the development of high-voltage engineering, integration circuit technology in semiconductor device electronics, and so on were very important R&D subjects in industries and universities in Japan. In that situation, characterization of electronic and electrical properties of materials and electronic devices being subjected to electric field under operational conditions was urgent task. For this purpose, TSC method was chosen as one of useful ways in research laboratories and in industries, and this method had made a great contribution to the development of electrical insulation engineering. Also this method had been widely applied to characterize bulk and interface properties of electronic devices such as metal-insulator-Si-semiconductor (MIS) diodes and metal-Nitride-Oxide–Si-semiconductor (MNOS) devices. At the same time, experimental TSC technique and analytical TSC method for studying carrier behaviors in solids and in devices had greatly advanced, and many important books and review articles on TSC method were published [1-4].

On the other hand, during the past several ten years, many new molecules have been discovered, and also lots of advanced functional materials such as organic semiconductor materials, ferroelectric materials, biomaterials, ceramics etc. have been developed [5,6]. The discovery of new molecules and emergence of novel materials have highly motivated researchers to utilize them in the research fields of electronics, electrical engineering, chemical engineering, medical engineering and so forth. In this situation, TSC measurement has attracted much attention in industries and in academia as a tool for characterizing new materials and devices using novel materials. It is instructive here to note that recent developed materials are never materials as replacement of classical ones such as polyethylene and Si-semiconductor, and they have potentiality to open new research fields such as organic materials electronics, molecular electronics, bioelectronics, and others. This means that there are many new technical and scientific issues we should explore for utilizing the TSC method to characterize new materials and novel devices. This review reports the latest research trend in TSC method for development of materials and devices in Japan [7, 8].

2. TSC and TSC method

2.1 Origin of TSC

We here briefly discuss the principle of TSC and TSC measurement [1-4, 7]. As mentioned in section 1, TSC is short circuit current, and it flows through samples during heating due to displacement of positive and negative charges, rotational motion of permanent dipoles, and so forth. By heating, trapped carriers, dipoles, ions so on are thermally activated, depending on material properties. This material dependent thermal process is characterized by a physical quantity $+H$ called as activation energy, and it proceeds with characteristic time τ given by $\tau = \tau_0 \exp(+H / kT)$ (: relaxation time). Here, τ_0 is pre exponential factor, k is Boltzmann constant, and T is absolute temperature. The activation energy $+H$ represents depth of carrier traps E_t for TSCs due to trapped carriers, whereas it represents barrier height for rotational motion of dipoles for TSCs due to dipolar depolarization. Therefore it is very important to determine the activation energy to study material properties. Fig. 1 plots the relationship between $\ln \tau$ and $1/T$. This linear relationship suggests that the activation process proceeds very rapidly at high temperatures, whereas it proceeds very slowly at low temperatures. TSC measurement makes use well of this $\ln \tau$ - $1/T$ relationship, and many methods have been developed to determine the activation energy $+H$ and relaxation time τ from TSC curves during the last several decades [1-4, 7,8].

For typical TSC measurement, firstly samples are biased at high temperatures to induce polarization in samples in very short time by applying *d.c.* voltage to samples, where this polarization includes carrier trapping in samples by injected electrons and holes, dipolar polarization, interfacial polarization, ionic polarization and others. Subsequently, samples are very rapidly cooled to low temperatures to freeze the polarization, with taking into account the $\ln \tau$ - $1/T$ relationship (see Fig.1). After that, samples are electrically shorted. Subsequently they are heated at a constant heating rate β. Note that heating rate does not need to keep constant for TSC measurement, but use of constant heating rate makes easy TSC analysis and thus constant heating is most often used in measurement. During thermal heating, short circuit current flowing through sample is measured. This short circuit current is TSC. Noteworthy that photo-radiation, X-ray radiation so on are available instead of *d.c.* biasing, to study degradations, defects, and so forth.

Figure 2 illustrates an example of TSCs from polyethylene film stressed by *d.c*. biasing, where several TSC peaks are observed with increase of temperature [9]. Interestingly some TSC peaks (Peaks A and B) are positively generated in the direction of depolarization, i.e., in the direction of discharging, but there is a TSC peak (Peak C) that is negatively generated in the polarization direction, i.e., in the direction of charging. One may wonder why TSC flows in the way as illustrated in Fig.2. Of course, we discuss the results by assuming that TSC flows due to discharging during

heating, that is, the film stressed by *d.c.* biasing will return to the initial state by heating and charge distribution in films formed by *d.c.* biasing will return to the initial state before stress biasing. However, it will be hard to explain physical reasoning of the appearance of the TSC peaks generated negatively, in the direction of charging. Because our general accepted idea coming out from the charging and discharging of ideal capacitor might be as follows; discharging current flows in opposite direction with charging current. To answer this question, we need to discuss the direction of carrier movement in short-circuit sample in terms of electric field distribution in the sample, because carriers will be conveyed by the electric field formed in samples. The physical reasoning of the negative TSC is explained in the next paragraph and in Sect. 2.2.

Figure 3 illustrates the principle of TSC, where a film with a thickness of d is sandwiched between two parallel electrodes 1 and 2, and the film is placed in a closed short circuit with an ammeter. According to the electro-magnetism theory, if charge $+q$ located inside of the film displaces with a distance of Δx in the film thickness direction, in a manner as illustrated in Fig. 3(a), the amount of charge of $+q\frac{\Delta x}{d}$ flows through the ammeter (see Appendix). That is, the displacement Δx of charge $+q$ is definitely the origin of TSC. The displacement Δx of charge $+q$ happens in the region $-d \le \Delta x \le +d$. Here $\Delta x = -d$ represents the situation when charge $+q$ moves from electrode 2 to electrode 1, whereas $\Delta x = +d$ represents the situation when charge $+q$ moves from electrode 1 to electrode 2.

For dipolar rotational motion, the original position of dipoles is fixed inside of the film, but the rotational motion of dipoles is equivalent to the displacement of charge $+q$ with a distance of $\Delta x = +l$ or $-l$ in the film thickness direction, where $\mu = ql$ (permanent dipole moment) (see Fig.3(b)). That is, due to the rotational motion of one dipole, the amount of charge given by $\pm\frac{\mu}{d}$ flows through the ammeter.

2.2 TSC curves

For TSCs due to dipolar depolarization in films sandwiched between two identical electrodes, the external electric field caused by external voltage is formed in films, but with no space charge field if merely dipolar polarization is formed in films. Consequently, in short circuit condition with zero-external voltage, merely dipolar rotation due to dipolar depolarization happens during heating. In this case, dipoles rotate and go back to the initial state, and finally the dipolar polarization P_0 which is initially formed in films disappears. This means that the displacement of charge Δx in discharging process occurs just in the opposite way to the polarization process.

Consequently, TSCs are generated in the opposite direction to the charging direction. The two TSC peaks (Peaks A and B) observed in the lower temperature region in Fig.2 corresponds to this process.

On the other hand, for TSCs due to de-trapping of electrons and holes in film sandwiched between two identical electrodes, the situation is quite different and rather complex, where space charge field formed in films due to trapped charges makes a significant contribution for the transport of thermally released electrons and holes. Space charge field is formed in films due to carrier injection from electrodes by *d.c.* biasing. For example, a potential hill is built in film after shorting film at low temperatures, due to the presence of excessive trapped charges (see Fig.4). As released carriers move along the electric field, the carrier transfer direction depends on the position of the carriers released with respect to the position of the potential hill. Consequently, TSC current flows according to the movement of the position of the potential hill which corresponds to the so-called zero-field position [10]. This means that a part of released carriers in film move to the discharging direction, whereas others can move to the charging direction. Accordingly, it is possible that TSC flows in the charging direction, in a manner as shown in the higher temperature region of Fig.2 (Peak C). In a special case, we anticipate no generation of TSC peaks. Therefore, for analyzing TSCs due to trapped carriers, techniques that can control the transport direction of released carriers are useful. Among them are a technique using *collecting voltage* [11] and a technique using *blocking layer* [3, 4, 7].

A typical TSC curve due to dipolar depolarization is described as [1-4]

$$TSC(T) = \frac{P_0}{\tau_0} \exp\left\{-\frac{H}{kT}\right\} \exp\left\{-\frac{1}{\tau_0 \beta} \int_{T_0}^{T} \exp(-\frac{H}{kT}) dT\right\}, \tag{1}$$

where P_0 is initial polarization formed in samples by *d.c.* biasing, k is Boltzmann constant, T is temperature given by $T = \beta t + T_0$ (β : constant heating rate, t : time, T_0 : initial temperature). TSC appears as illustrated in Fig. 5 with one peak at a temperature $T=T_m$ (Maximum temperature). Here the relation $\tau(Tm) = \tau_0 \exp\left\{+\frac{H}{kT_m}\right\} = \frac{kT_m^{\,2}}{\beta H}$ is satisfied at $T=T_m$. In the TSC measurement, TSC flows due to depolarization of the initial polarization. Consequently, the following relation is satisfied when TSC is measured using electrically shorted circuit.

$$P_0 = \frac{1}{\beta}\int_{T_0}^{T_\infty} TSC(T)dT \tag{2}$$

On the other hand P_0 is given as

$$P_0 = \frac{N\mu^2}{3kT_b}E_b, \tag{3}$$

where N is density of dipoles per volume, T_b is biasing temperature, and E_b is external electric field used for biasing. If we apply external electric field E_c during heating in TSC measurement, E_b in eq.(3) should be replaced by $E_b - E_c$. That is for TSCs due to dipolar depolarization, external applied electric field is acting to change polarization formed in samples.

On the other hand, TSCs due to trapped carriers are ruled by carrier de-trapping process and succeeding carrier transporting process. If carrier de-trapping process takes much longer time than carrier transport process, TSC is governed by carrier emission process by heating (emission limited process) and the TSC equation is described as [2-4]

$$TSC(T) = A\nu \exp\left\{-\frac{E_t}{kT}\right\}\exp\left\{-\frac{\nu}{\beta}\int_{T_0}^{T}\exp(-\frac{E_t}{kT})dT\right\}, \tag{4}$$

where ν is attempt to escape frequency of trapped charges. Eq.(4) is very similar to eq.(1), suggesting that TSC due to trapped carriers can be analyzed in the manner same as that for TSCs due to dipolar depolarization. Noteworthy that A represents the total charge recorded by an ammeter in TSC measurement, but this is not the total charge qN_t trapped in samples. As mentioned in section 2.1, the recorded TSC current is displacement current, and it depends on the direction and displacement of trapped charges in samples during heating. For example, if trapped carriers are homogeneously trapped in samples spatially and all of the de-trapped carriers are transported to one electrode, $A = qN_t/2$. It is most probable that trapped carriers in samples are transferred to both electrodes due to the presence of space charge field, and results in

$-qN_t \le A \le qN_t$. Noteworthy that applied collecting electric field E_c is employed in TSC measurement to modify the space charge field in samples. That is, by applying an appropriate collecting electric field E_c , we can convey all de-trapped carriers to the direction of one electrode.

On the one hand, if it takes much longer time for carrier transport in comparison with the carrier de-trapping process, TSC formula should differ from eq.(4) and TSC is ruled by carrier transport process (transport limited process). Consequently, TSC should be dependent on the temperature dependence of carrier mobility [7].

For TSCs due to interfacial trapped charges such as in MIS diodes, charges de-trapped by thermal emission cannot cross over the insulator layer. That is; the insulating layer is serving as *a blocking layer* and blocks charges emitted from traps to cross the layer, and all de-trapped charges are forced to move in the direction to the semiconductor layer from the semiconductor-insulator interface. Accordingly, if interfacial charge emission governs the TSC process during heating (emission limited process), TSC is approximately given by [7]

$$TSC(T) \propto \beta \frac{dQss}{dT} + \beta \frac{dQs}{dT}. \qquad (5)$$

If the contribution of the change of the charge Q_s in depletion layer (2nd term) is minor, change of interfacial charge Q_{ss} makes a main contribution of TSC. Change of Q_{ss} with temperature (the first term of eq.(5)) represents thermal emission process of charges from traps. As that TSC due to emitted charges from a trap with a depth of E_t is described in the way same as eq.(4). Generally, interfacial states are broadly distributed energetically in the energy gap of semiconductor and TSC peak temperature T_m shifts in accordance with the depth of carrier trapping state. Thus TSC can probe trapped charge profile at interfacial energy state of MIS diodes [12-14].

As mentioned above, we briefly discussed TSCs due to dipolar depolarization, carrier de-trapping, and thermal emission from the interface. Of course, there are other TSCs, e.g., TSC due to ionic carrier motion, TSC due to long-range motion of impurity ions, TSC due to phase transition, and others. Therefore, TSC method is available for studying charge motions in materials and devices, if we can identify the origin of TSCs.

3. TSC study trend in Japan

As mentioned in earlier section 2, thermally stimulated current (TSC) measurement is very

simple, but we can get useful information on carrier trapping, polarization and others in a variety of materials, including dielectrics, ferroelectrics, semiconductors, ceramics, plastics, and so on. Recent development of new advanced materials and technologies have motivated researchers to utilize TSC measurement as a tool of characterizing new materials and new devices, in terms of electrical properties of materials, and device performance and its reliability. Among them are evaluation of defect states of advanced electronic materials, of structure of nano-enabled materials, and of performance of organic and inorganic devices such as functional oxide devices, C60 FETs, organic LEDs, emerging photovoltaic cells, etc. As a result we can see many TSC reports in scientific journals. In the followings, we briefly discuss TSC study trend in Japan.

3.1 Analysis of dipolar TSC for development of advanced materials

As mentioned in earlier sections, TSC study is growing with the emergence of new and advanced materials. Water is very important for our daily life, and also it is important for production in industry, and so forth. Accordingly, much attention has been paid to the behavior of water itself, i.e., water molecules in biomaterials, polymers, so forth. The fundamental TSC study on water is being carried out using ice of waters, ion exchanged waters, so on [15]. These TSCs show dipolar behavior that follows eq.(1), and their peak positions clearly reflect the difference between the structure of pure water and heavy water, and the contribution of ions such as K+ ,Na+, Li+ , Ca++, Mg++, etc. Also the contribution of water molecules in polymers such as Nylon 66 have been intensively studied, in terms of the molecular structure of polymers, for further development of advanced functional polymers [16]. Noteworthy that from view point of TSC experimental technique it is of great progress in that we can get TSC spectra of ice of waters with high sensitivity.

With the development of advanced ionic ceramics, TSC is attracted much attention in the field of ceramics. Ionic ceramics such as hydroxyapatite (Ca10 [PO4]6 [OH]2) are being studied by using TSC, in terms of polarization originated from protons [17]. Dipolar motion of protons greatly effects on TSCs, and four types of polarization have been identified in the wide range of temperatures. The successful finding of these four polarizations is greatly due to the progress of TSC experimental technique and its analytical method.

In the field of telecommunication technologies, TSC is attracted much attention as a tool of evaluation method of degradation and deterioration of electro-optic (EO) polymers. In this research field, development of new EO polymers that are available for long-term is an urgent task. Generally it takes much longer time to evaluate degradation by using isotherm measurement, because the relaxation time of polarized dipoles in EO polymers is much longer at room temperature. TSC method has a potentiality to overcome this situation. By using EO polymers, disperse Red 1 (DR1)/poly(methyl methacrylate) (PMMA) guest/host polymer, side-chain

copolymer DR1–PMMA (PMMA-co-DR1) etc., dipolar depolarization in EO polymers has been examined by TSC measurement, and characteristic time τ given by $\tau = \tau_0 \exp(+H / kT)$ (: relaxation time) was determined as an index of thermal stability of EO polymers [18]. The time required for the determination of τ by TSC measurement is much shorter than that by isothermal measurement such as potential decay measurement at room temperature. Consequently, the information of relaxation time is promptly available for improvement and redesign of new EO polymers. The determination of relaxation time τ by TSC measurement is now getting a new tool for the development of advanced thermally stable EO polymers.

As mentioned above many TSC experiments are being carried out in a variety of new research fields, on focusing TSC spectra due to dipolar depolarization.

3.2 Analysis of traps and defects

3.2.1 Organic devices

Presence of carrier traps, defects, interface-states is a serious problem for electronic devices, sensors, etc. For analyzing these traps, defects, etc., in terms of lifetime of device and degradation of materials, TSCs are employed in the R&D along with development of new organic semiconductor materials, new devices, etc. Among them are TSC studies on new organic materials [19,20], carrier traps and defects of Organic Light Emitting Diodes (OLED) [21], Pentacene Schottky diodes [22], Organic field effect transistors (OFETs) [23], Organic Solar cells (OSCs) [24,25], and so on. In these TSC studies, basically eq. (4) is used in the analysis under assumption that thermal emission process governs TSCs. TSC measurements well identify traps and defects of these devices, and account for the influence of water, oxygen, photo- and high energy-particle radiation etc. on the device performance. That is, TSC is well utilized to identify the trap depth, and changes of trap density, etc. For example, for AlQ3 layer in EL devices, it was shown that the trap density of deep traps increases with degradation, and the presence of electron traps in α – NPD layer and of electron and hole traps in Alq3 layer have been identified [21]. Also for the application of new materials to devices, impurity of the materials and carrier traps are very sensitive to device performance. For this purpose TSC has been employed for analyzing influence of impurities on the efficiency of OSCs using C60, and the relationship between the trap density and impurities of C60 has been studied. OSC efficiency is shown extremely improved about 22% due to increase of purification from 99.95 to 99.999%, but the trap density of C60 films evaluated by TSC shows no significant dependence on impurities of C60 in this high purity region. This result suggested that the improvement of interfacial device structure such as flatness is a key parameter for increase the efficiency of OSCs with C60, and further purification is

unnecessary [24]. Perovskite is one of hot-topic materials in the field of solar batteries, but its degradation is a very serious problem for practical use. In this research field TSC has been employed for studying the degradation mechanism of perovskite, and it has been demonstrated that residual water molecules in perovskite is an origin of hole traps that results in degradation [25] . In this way, for the development of new organic devices using new functional materials such as Alq3, C60, perovskite and so on, TSC is being well utilized.

TSC measurement has been widely used to study interfacial states of MIS diode and also field effect transistors. In earlier days, main devices were Si-based MOS diodes, transistors and other inorganic devices, and TSC was employed to study interface-states of these devices [12, 14, 26]. Main reason is that the interface property rules the device performance, and thus analysis of semiconductor-insulator interface is very important for the improvement of device performance. Nowadays, TSC measurement is being used to evaluate organic diodes, OFETs and so on [20, 23, 27]. Again interface is a key issue of organic devices. Generally, MIS structure is used to study interface-states between insulator and semiconductor, but for organic semiconductor devices discrimination of hole and electron traps is quite a task, and carrier transport of OFETs greatly depends on the quality of interface. That is, owing to ambiguity of polarity of carrier species, e.g., holes or electrons, and the device performance different from conventional Si-based devices, etc., we need to carry TSC experiments with consideration of specific properties of organic semiconductor devices, though the TSC technique employed for analyzing organic devices is very similar to the technique that has been used for analyzing conventional Si-based devices. Accordingly, besides TSC measurement using organic MIS diodes, TSC measurement is also directly employed for OFETs [23]. For TSC measurement of OFETs, by choosing polarity of applied gate-voltage we can selectively investigate electron and hole behaviors in devices, and also can study electron- and hole-traps and defects in channel region of OFETs. As organic semiconductor materials, pentacene [23], TCNQ [20], and so on are used, and insulator-semiconductor interface properties are analyzed by using TSC, and interfacial energy states, density of interface states, density of defects etc. are well evaluated.

3.2.2 Inorganic devices

TSC measurement is also used for inorganic semiconductors. Wide-gap semiconductors such as GaN, SiC and ZnO are anticipated for use as High-speed devices, High-power devices, and optoelectronic devices, and many investigations are extensively being carried out. However defects, radiation effects are key issues for practical applications. Accordingly, TSC measurement is employed to evaluate energy levels of trap, trap density, and defects induced by photo- and particle- radiation in the bulk of these semiconductors [28-30]. The technique used for TSC measurement is basically the same with other cases of TSC measurement, but the TSC system is

designed so that photo radiation etc. can carry at low temperatures. Samples used for experiments are semiconductors, the energy level is evaluated from the slope of $1/T_m - \ln\left(T_m^{\,4}/\beta\right)$ plots by carrying experiments at various heating rates β, on the basis of the relation called as Look's relation [31]. Noteworthy that the energy level of traps in polymers, etc. is generally evaluated from the slope of $1/T_m - \ln\left(T_m^{\,2}/\beta\right)$ plots, where the temperature dependence of effective carrier density Nc is presumably constant. As mentioned above TSC measurement is well used for analyzing wide-gap semiconductors [1-4].

PZT is ferroelectric materials and it is used as materials for memory devices. To study defects of such ferroelectric materials, TSC measurement has been carried out. In the TSC measurement TSC peaks due to spontaneous polarization appears and also leakage current flows across PZT materials. These contributions observed in PZT are removed experimentally from the TSC spectra by using thermal cleaning method etc. and carrier traps are extensively studied [32-35].

As mentioned in section 3.2.1 and 3.2.2, in the application of materials to electronic components, materials are subjected to applied *d.c.* electric field and also external environment stimuli such as radiation, water, light, etc. Accordingly, defects and carrier traps give direct influence on material's electrical and electronic properties, and device performance. TSC measurement is well utilized to characterize materials and devices, on focusing carrier traps.

4. Development of TSC technology

Thermally stimulated current is very small and it is generally less than 1 pA. Therefore it is quite important to use instruments and circuits that can measure such small currents. Measuring-instruments and circuits must be designed to be free from mechanical noise and electrical noise. Highly insulating materials are used as electric cables for the electrical circuit, and many noise sources such as frictional charge induced by friction, capacitance changes induced by vibrations, and so forth are removed. Nowadays we can measure very small current with high reproducibility by setting samples in a faraday cage, and connecting to an electro ammeter. In other words, knowledge of electrostatic phenomena is quite important to establish TSC measurement, and the TSC experimental technology is advancing to measure very small current by removing noises [36-38]

Analytical technique of TSC is also advancing. Basically TSC analysis is carried out by using eq.(1), but in actual case of TSCs many TSC peaks overlaps each other. Consequently, techniques that can discriminate TSC peaks from one original TSC curve are essentially important for

analyzing TSCs. Experimentally it can be done by employing partial heating method as well as thermal cleaning method [1,4], and these are widely used. From viewpoint of analytical method, many techniques have been introduced. Among them are curve fitting method, Bucci's plots (whole curve method) and so on [1, 4, 7]. These techniques have been developed on the basis of TSC formula Eq.(1). Nevertheless these are still not sufficient to discriminate overlapped TSC peaks from the original TSC curve. On the basis of advanced computer technology, new analytical methods have been developed in Japan. Among them are Asymptotic Estimation Method (AEM) [39] , Maximum Entropy Method (MEM) [40], and others. By using these methods activation energy and other TSC parameters are definitely determined. By employing MEM for analyzing MIS capacitors with a structure of Al/Si_aN_b/Si, TSCs due to single electron de- trapping from single trap has been well discriminated [40].

In this way TSC technology is advancing experimentally and analytically on the basis of computer technology.

5. TSC measurement coupled with other experimental method

As mentioned in section 2, TSC is short circuit current, and it is basically displacement current. This current is generated due to carrier motion in samples, such as orientational motion of dipoles, carrier de-trapping and so on, and it flows through an external ammeter. Consequently, we can speculate carrier motions in samples from the trace of recorded current. In other words we merely probe carrier motions indirectly from the recorded TSC curve. Accordingly, it is difficult to distinguish electron movement and hole movement in a single film sandwiched between identical parallel two electrodes. It is of great help to develop a TSC technique that can directly probe carrier motions by coupling other experimental technique [41,42]. TSC technique coupled with optical second harmonic generation method (SHG) has been developed and it has been used to study dipolar motions in thin films [43], and recently it has been applied to study interfacial states of OLED and organic MIS diodes by coupling TSC measurement with electric field induced second harmonic second generation method (EFISHG) [41].

6. Conclusions and Future scope

Recent progress of TSC measurement has been briefly reviewed. We can see TSC studies in a variety of research fields, and experimental techniques and analytical methods are developing accordingly. TSC is short circuit current, and it can be measured by using one electro-ammeter. Many new materials will be continuously discovered and developed in future. We therefore believe TSC technique will serve as one of key techniques to characterize these materials in future. With consideration of this situation, we anticipate TSC should be standardized so that every researcher can use it, easily and reproducibly. TSC measuring method of plastic films has been

standardized as JIS K7131 in Japan [44], but it is basically for detecting TSCs due to dipolar depolarization and it is no longer sufficient. It will be necessary to standardize TSC measuring method for measuring TSC due to carrier de-trapping, etc. Along with globalization, activity for standardization of TSC is on- going, on focusing evaluation of carrier traps of electronics devices in Japan [45].

Appendix

Figure A illustrates the principle of TSC measurement. In Fig.A-1, there is no charge in the film and also no induced charge on electrodes. In Fig.A-2 charge $+q$ is apart just right from electrode 1 ($x = 0$) with a negligibly small distance $x = +\delta$, at the film surface. Owing to the charge neutrality of the system, charge $q_1 = -q$ appears on electrode 1, but still no charge on electrode 2, i.e. $q_2 = 0$. That is, as the positive charge $+q$ and the negative charge $-q$ are separated with a very small distance δ, electric flux diverging from the charge $+q$ totally falls on the charge $-q$ on electrode 1 As a result, there is no possibility current flows through an ammeter and $q_2 = 0$. In Fig.A-3, charge $+q$ is displaced from the position at $x = +\delta$ to $x = x$., *i.e.* $\Delta x \approx x$, To meet the requirement of electro-static charge distribution in short-circuit condition, electric flux diverging from the positive charge $+q$ falls on both electrodes, and non-zero charges q_1 and q_2 are induced on electrodes 1 and 2, respectively. This means, whilst charge $+q$ is displaced from the position at $x = 0$ to $x = x$, q_2 flows from electrode 1 to electrode 2 along the external circuit through an ammeter, i.e. initial induced charge $q_1 = -q$ on electrode (see Fig.A-2) decreases to

$$q_1 = -q - q_2$$

This situation can be illustrated using equivalent capacitors C_1 and C_2 (see Fig.A-4). Owing to the presence of charge $+q$ at $x = x$, potential $V_x = \dfrac{+q}{C_1 + C_2}$ is built at this position, and charges $q_1 = -C_1 V_x$ and $q_2 = -C_2 V_x$ are electrostatically induced on electrodes 1 and 2, respectively. That is, charges $q_1 = -\dfrac{d-x}{d} q$ and $q_2 = -\dfrac{x}{d} q$ are induced on electrodes 1 and 2, respectively.

From the discussion above, we can say that TSCs recorded by an ammeter is dependent on the trace of displacement of charge, and if charge $+q$ displaces with a distance Δx inside of the film from $x = x$ to $x = x + \Delta x$, change of q_2, i.e. Δq_2, is given by $-q\frac{\Delta x}{d}$.

The displacement of charges is strongly dependent on the electric field formed in films. As a result, it may happen that TSC flows in the direction same as the charging direction (see Fig.2, Peak C) when TSC traces carriers that are being de-trapped from films, owing to the space charge field formed in films by stress-biasing.

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Figure Captions

Figure 1 $\ln \tau$ -$1/T$ plots

Figure 2 A typical example of TSC of polyethylene (PE) film. The film thickness is 40 μm. The PE film was stressed biased at Vb= 5,000 V. (A part of Japanese tiles have been translated to English and reprinted with permission from Ref. 9. (c) 1975 Institute of Electrical Engineers of Japan)

Figure 3 Principle of TSC. (a) Displacement of charge +q at a distance of Δx, and the amount of charge flowing through an ammeter $+q\frac{\Delta x}{d}$. (b) Rotational motion of dipole $\mu = ql$ (permanent dipole moment) and the charge flowing through ammeter $\pm\frac{\mu}{d}$.

Figure 4. Distribution of trapped electrons and a potential hill built in film. x^* represents the position of potential hill (zero-field position). Thermally de-trapped electrons in the region between $0 < x < x^*$ move to electrode 1, whereas thermally de-trapped electrons in the region between $x^* \leq x < d$ move to electrode 2. The de-trapping process of trapped holes can be explained in the same way where polarity of electrostatic potential is opposite.

Figure 5 A typical TSC curve computed using eq.(1), where H= 1.0 eV and τ_0=1.0×10^{-15} s.

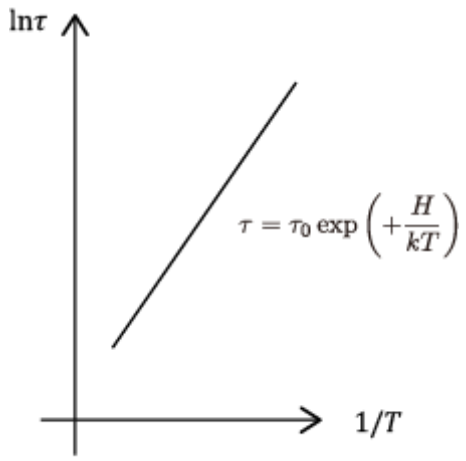

Figure 1 M. Iwamoto et al.

Figure 2 M. Iwamoto et al.

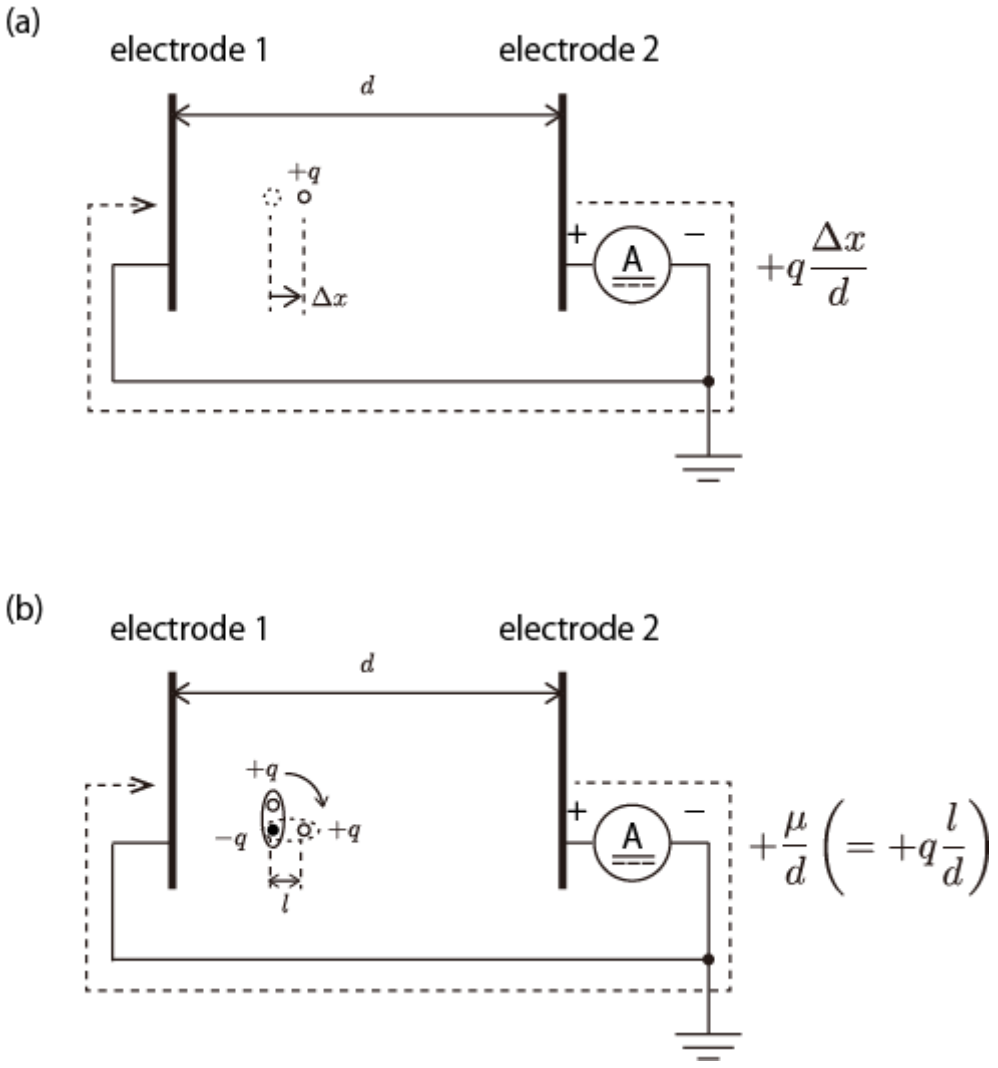

Figure 3 M. Iwamoto et al.

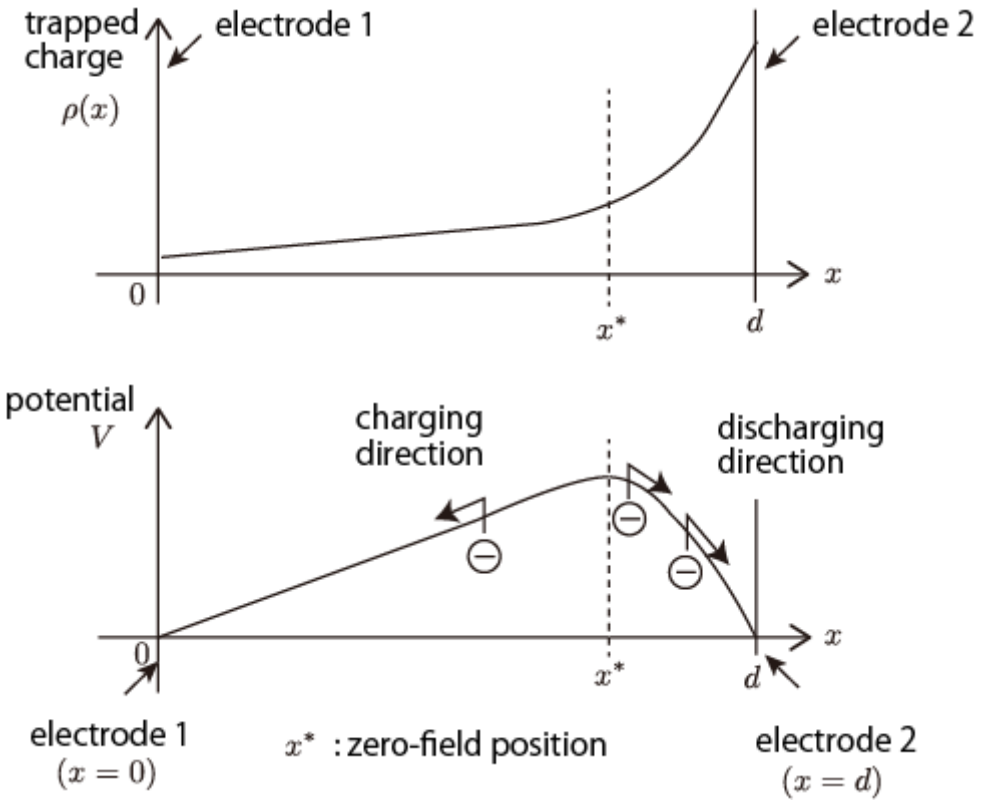

Figure 4 M. Iwamoto et al.

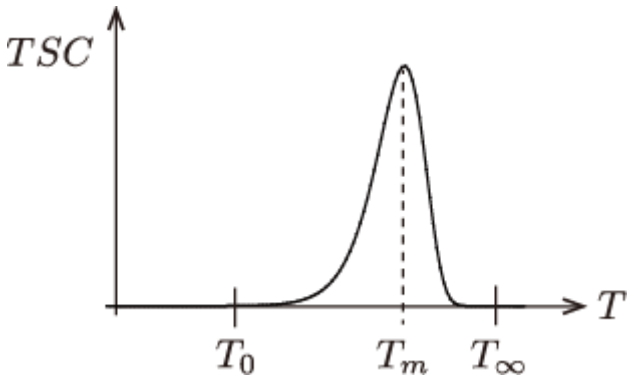

Figure 5 M. Iwamoto et al.

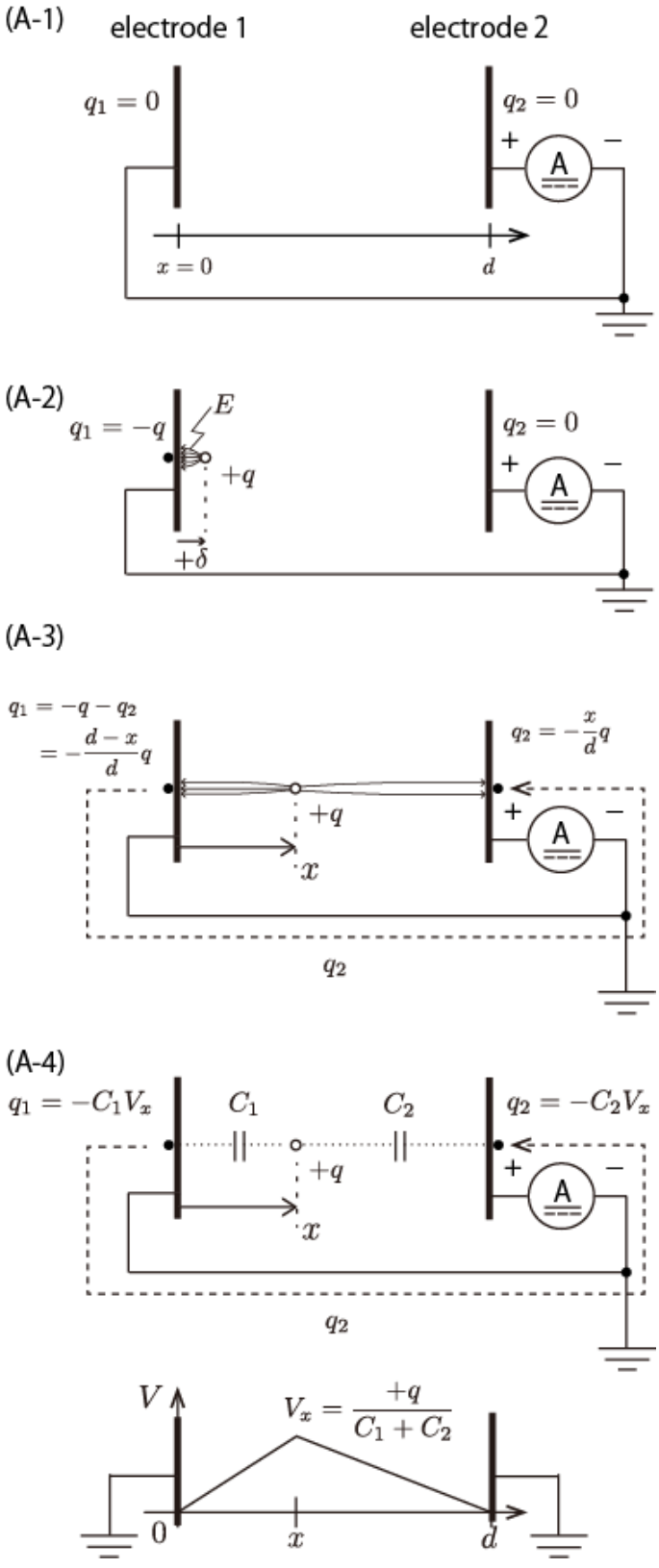

Figure A M. Iwamoto et al.