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Band-gap narrowing in -(Cr_xFe_{1-x})_2O_3 solid-solution films

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Band-gap narrowing in $\alpha$-(Cr$_{x}$Fe$_{1-x}$)$_2$O$_3$ solid-solution films

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We report on structural and optical properties for the (0001)-oriented $\alpha$-(Cr$_{x}$Fe$_{1-x}$)$_2$O$_3$ ($0 \leq x \leq 1$) epitaxial films prepared on c-sapphire substrates by using pulsed-laser deposition. Pure corundum phase with atomically flat surface was obtained in the entire composition range. Optical absorption spectra for the films with $0.2 < x < 0.9$ showed a nearly constant band-gap (1.7 eV), which is narrower than those of $\alpha$-Fe$_2$O$_3$ (2.1 eV) and $\alpha$-Cr$_2$O$_3$ (3.0 eV). The result suggests that the band-gap narrowing arises from a type-II band alignment of these oxides and the fundamental band-gap lies between the Cr $t_{2g}$ and O 2$p$ occupied states and the Fe $t_{2g}^*$ empty state. © 2011 American Institute of Physics. [doi:10.1063/1.3669704]

Aspects of visible light-driven photocatalysts have been widely studied to alleviate global warming upon development of sustainable energy production, including the water splitting and the artificial photosynthesis. At present, the method of sustainable energy production, including the water splitting and the artificial photosynthesis, is widely studied to alleviate global warming upon development of sustainable energy production. However, the efficiency of these processes is limited by the low absorption of sunlight. Indeed, we have observed red-shift of the absorption edge in our samples. The $\alpha$-(Cr$_{x}$Fe$_{1-x}$)$_2$O$_3$ thin films were grown on c-plane sapphire substrates by using an ultrahigh vacuum pulsed-laser deposition system and a KrF excimer laser. The substrates were annealed at 1100°C for 3 h in air to obtain atomically flat surfaces. The film composition was varied with using sintered ceramics targets having different compositions of $x = 0$, 0.25, 0.50, 0.74, and 1. In addition, films with intermediate compositions were prepared by repeating alternate ablation of two neighboring targets. The best crystalline quality was reproducibly obtained under the following condition. The repetition and fluence of the laser were 10 Hz and 0.9 J/cm$^2$, respectively. Growth temperature was 740°C and chamber pressure was a constant of 1 mTorr while flowing pure oxygen gas. Film thickness was regulated to be 40–80 nm. After the growth, the films were annealed at 1000°C for 1 h in air. The film morphology and crystal structure were characterized by means of atomic force microscopy (AFM) and x-ray diffraction (XRD), respectively. The optical properties were investigated by UV-Vis-IR spectroscopy at room temperature. The film composition was analyzed for all the films by using a scanning electron microscopy equipped with an electron probe microanalyzer (EPMA). The composition of catalysts was confirmed to be identical to those of the targets and/
or the compositions deduced from ratios of deposition rates and number of laser pulses for one to another target (the intermediate compositions), regardless of growth condition.

All the films were epitaxially grown along the $c$-axis with a single domain $(\{11\overline{2}0\} \times (\overline{1}1\overline{2}0))_2\text{CrFe}_x\text{O}_6//\{11\overline{2}0\} \times (\overline{1}1\overline{2}0)$, whereas some of the as-grown films indicated a secondary phase, which was identified as the $(111)$-oriented spinel structure. After the annealing, the spinel phase was completely transformed to the corundum phase as formal valence of Fe ions changed from $2^+$ to $3^+$. Representative result is shown in Fig. 2 for the $\alpha$-$\text{CrFeO}_3$ ($x = 0.5$) film. The surface became atomically flat after the annealing as verified from clear Laue fringes, as well as the AFM image (shown in inset). The height of surface steps was $0.46$–$1.12$ nm, corresponding to multiple layers of the charge neutral unit $(\frac{c}{6} \approx 0.23$ nm). We emphasize that these features are essential to analyzing subtle difference in absorption spectra, making effects of interference and scattering negligible.

The $a$- and $c$- axes lattice parameters were evaluated from the $(0006)$ and $(10\overline{1}4)$ reflections. The composition dependence of lattice parameters is plotted in the top panel of Fig. 3. A good agreement with values for powder samples (broken lines adapted from Ref. 14) indicates that high-quality and relaxed films were obtained in the entire range of composition. As shown in the bottom panel of Fig. 3, unit cell volume systematically decreased as Cr content increased, which is consistent with difference in ionic radii of Fe$^{3+}$ ($0.645$ Å) and Cr$^{3+}$ ($0.615$ Å).

Figure 4(a) shows absorption spectra of the $\alpha$-$\text{CrFe}_x\text{O}_3$ films. We took the first and second derivatives of the spectra to identify individual absorption bands as apparent peaks and/or shoulders. Figure 4(b) represents a central result of this study: all traces for characteristic absorption bands indicate complicated composition dependencies beyond the extent that a compound semiconductor solid-solution indicates large bowing behavior. Moreover, the emergence of shoulders at approximately $1.8$ eV ($\Delta$) is consistent with the aforementioned type-II band alignment. Direct and indirect band-gaps of corresponding samples were evaluated to be $2.1$ eV and $1.7$ eV, respectively [See Fig. 4(c)], assuming the
following relation: \( \alpha \propto (h\nu - E_g)^n \) (Ref. 16), where \( \alpha \) and \( h\nu \) are absorption coefficient and photon energy, respectively, and \( n \) is either 2 (indirect) or 1/2 (direct). These values (indirect and direct \( E_g \)) are compared with those for \( \alpha\text{-Fe}_2\text{O}_3 \) (2.1 eV and 2.2 eV) and \( \alpha\text{-Cr}_2\text{O}_3 \) (3.0 eV and 3.2 eV).

Having established systematic change in absorption spectra, we discuss the origins of each transition. As for \( \alpha\text{-Fe}_2\text{O}_3 \), fundamental absorption edge corresponds to a CT transition from O 2p states to Fe t\(_{2g}\) states, which gradually evolves to the UV region showing a complex spectral shape. As for \( \alpha\text{-Cr}_2\text{O}_3 \), discrete peaks at 2.1 eV (\( \bigotimes \)) and 2.7 eV (\( \bigtriangleup \)) is attributed to \( d-d \) transitions as \( ^4T_{2g} \leftarrow ^4A_{2g} \) and \( ^4T_{1g} \) (F) \( \leftarrow ^4A_{2g} \), respectively.\(^{11,17} \) The CT transition from O 2p states gives a broad shoulder at 3.4 eV.\(^{11} \) A maximum at 4.5 eV is assignable to a \( d-d \) transition as \( ^4T_{1g} \) (P) \( \leftarrow ^4A_{2g} \). For the solid-solution films, no apparent spectral weight transfer was observed, indicating significant overlaps of individual transitions. For example, one can see that the \( d-d \) transition of \( \text{Cr}_3 \)\(^{3+} \) at 2.7 eV (\( \bigtriangleup \)) gradually shifts with increasing \( x \) and eventually merges into the CT band in \( \alpha\text{-Fe}_2\text{O}_3 \). Systematic but independent variations in the transitions above 3 eV is presumably associated with change in the O 2p energy level.

Finally, we would like to discuss band-gap narrowing. According to literatures,\(^{9,17,18} \) the absorption band at 1.8 eV corresponds to excitation of valence electrons at \( \text{Cr} \) t\(_{2g}\) and/or O 2p states to the empty Fe t\(_{2g}\)\(^* \) state. This picture is further supported by a recent theoretical study based on density functional theory (DFT) calculations with a Hubbard \( U \)-term, which concludes that the band-gap of CrFeO\(_3\) is reduced to 1.9 eV.\(^{19} \) In order to develop active photocatalysts based on \( \alpha\text{-}x\text{-Cr}_2\text{O}_3 \), photocurrent measurements under visible light is now being conducted.

In summary, we have prepared high-quality (0001)-oriented \( \alpha\text{-}x\text{-}(\text{Cr}_{1-x}\text{Fe}_x)\text{O}_3 \) solid-solution films by using pulsed-laser deposition. The absence of miscibility gap allows us to study systematic variations of structural and optical properties in the entire range of composition. From careful analyses of absorption spectra, we have found that fundamental band-gap is 1.7 eV in a composition range from \( x = 0.2 \) to 0.9. The lowest energy transition can be attributed to charge transfer from \( \text{Cr} \) t\(_{2g}\) and O 2p states to Fe t\(_{2g}\)\(^* \) state. The use of high-quality epitaxial films will be a suitable approach to explore visible light-driven photocatalyst based on complex transition-metal oxides.

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