Novel Room Temperature Stable Electride \(12\text{SrO} \cdot 7\text{Al}_2\text{O}_3\) Thin Films: Fabrication, Optical and Electron Transport Properties

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12SrO \cdot 7\text{Al}_2\text{O}_3 \text{ (S12A7)} is a meta-stable phase in the system of SrO-Al\(_2\)O\(_3\) and has the isosstructur with 12CaO \cdot 7\text{Al}_2\text{O}_3 \text{ (C12A7)}, which is composed of sub-nanometer-sized cages with oxygen ions loosely engaged in the cages. This letter reports fabrication of polycrystalline thin films of insulating and metallic S12A7 electride thin films. The as-crystallized film was an electrical insulator, while light-induced persistent electronic conductance with a conductivity of \(\sim 1 \times 10^{-4} \text{ S cm}^{-1}\) at 300 K was realized in proton-implanted films. Higher conductivities of \(\sim 270 \text{ S cm}^{-1}\) were attained in the films subjected to a reduction treatment using an oxygen deficient amorphous film deposition. These behaviors are similar to those observed on C12A7. The present results suggest that S12A7 is another candidate material to explore electronic functions originating from a nanoporous structure embedded in a crystal structure.

Key-words: Electride, Nano-porous materials, Pulsed laser deposition, Ion implantation, Electrical and optical properties

1. Introduction

Electride\(^{1-4}\) is an ionic compound in which electrons work as anions. Since the anionic electrons are loosely bound in the anionic sites and delocalized to some extent, it is expected that electron-active functions based on the anionic electrons, such as electronic conduction and cold electron emission, are rendered in electride. Recently, a thermally and atmospherically stable electron was synthesized from a nanoporous crystal \(2\text{CaO} \cdot \text{7Al}_2\text{O}_3\) \text{ (C12A7)} by utilizing its built-in nano-cage structure.\(^{5}\) The crystal structure of C12A7 is composed of a positively charged \(\left[\text{Ca}_2\text{Al}_2\text{O}_6\right]^{2-}\) framework containing twelve crystalllographic cages with a diameter of \(\sim 0.4 \text{ nm}\) and two extra free \(\text{O}^{2-}\) ions accommodated in the cages (referred to as free \(\text{O}^{2-}\) ions).\(^{6}\) The free \(\text{O}^{2-}\) ions are replaced by other negative ions with similar ionic radius such as \(\text{OH}^{-}\), \(\text{F}^{-}\), and \(\text{H}^{2+}\). The \(\text{H}^{2+}\)-bearing C12A7 is converted to a persistent electronic conductor by ultraviolet (UV) light illumination. Further, several methods to replace the free \(\text{O}^{2-}\) ions with electrons have been developed, which lead to the formation of the C12A7 electrode. The resultant C12A7 electrode shows attractive electronic properties such as a low work function of \(2.4 \text{ eV}\), a metal-insulator transition, and a superconducting transition.\(^{10-12}\)

12SrO \cdot 7\text{Al}_2\text{O}_3 \text{ (S12A7)} is a meta-stable phase in the SrO-\(\text{Al}_2\text{O}_3\) system and has the same crystal structure as C12A7 does.\(^{13}\) It is suggested that S12A7 is also converted to an electron. Moreover, since S12A7 has larger lattice parameters \((a=1.233 \text{ nm})\) than C12A7 does \((a=1.199 \text{ nm})\), the cages in S12A7 would be possible to accommodate ions larger than the inner size of the cages in C12A7. It is also expected that the uptake and release of the caged anions are easier in S12A7 than in C12A7. The synthesis of bulk S12A7 was first carried out by a sol-gel method.\(^{15}\) Although thin films are also required for electronic applications, there is no report on thin film fabrication of S12A7. It is known that a sol-gel method can produce thin films, but such films, in general, have poor adhesion and poor uniformity.

In this paper, a pulsed laser deposition method (PLD) was employed to fabricate S12A7 films. For a standard PLD process, high-density S12A7 ceramics is required for a PLD target. Preparation of a high-density sintered body of S12A7 was, however, difficult because S12A7 decomposes into \(\text{SrO} \cdot \text{Al}_2\text{O}_3 \text{ (SA)}\) and \(3\text{SrO} \cdot \text{Al}_2\text{O}_3 \text{ (S3A)}\) phases at temperatures \(>1000 \text{C}\) even in its favorable moisture air atmosphere. Therefore, we first examined an indirect PLD process that does not need a S12A7 target. SrO and Al\(_2\)O\(_3\) layers were first deposited sequentially by PLD, and they were then thermally reacted by a post-annealing at \(600-800 \text{C}°\). As results, S12A7 thin films were obtained but the yield was poor. Therefore, we report the other approach in this paper. It was finally found that a PLD process using a pressed S12A7 pellet as a target and subsequent post-crystallization produced polycrystalline S12A7 thin films at good reproducibility. The S12A7 films thus fabricated were converted to electronic conductors by a proton implantation & UV-light illumination technique and a reduction treatment using a reductive film deposition.

2. Experimental

To fabricate the crystalline S12A7 films, amorphous S12A7 films were first deposited at room temperature (RT) by PLD. MgO \(\text{(100)}\) and \(\text{Y}_3\text{Al}_5\text{O}_{12}\) \text{(YAG)} \(\text{(100)}\) single-crystals were used for substrates because they have good lattice matching with S12A7. A green compact of S12A7, prepared by a solid state reaction \(^{16}\) of \(\gamma\text{-Al}_2\text{O}_3\) and \(\text{Sr(OH)}_2\); \(8\text{H}_2\text{O}\) and subsequent cold isostatic pressing, was used as a target. An ArF excimer laser (193 nm) was employed for ablating the S12A7 target. An \(\text{O}_2\) gas was introduced to the PLD chamber at the partial pressure of \(\sim 1 \times 10^{-3} \text{ Pa}\) during the depositions. Finally, the amorphous S12A7 films were subjected to a post-annealing treatment for crystalization at \(840 \text{C}\) for \(1 \text{ h}\) in moisture air.

Ion implantation is a method which fits well micro-electronics processes such as carrier doping.\(^{15}\) This is also true for carrier doping in oxide semiconductor thin films as reported to date.\(^{10-18}\) Protons were implanted into the S12A7 thin film \((\sim 1 \mu \text{m} \text{ in thickness})\) at a temperature \(600 \text{C}°\), with a fluence of \(2 \times 10^{17} \text{ cm}^{-2}\). The acceleration voltage was 80 kV and the dose rate of the ion beam was \(\sim 2 \mu \text{A} \text{ cm}^{-2}\). In order to reduce the sample charging by the implantation, the sample surface was covered with a metal plate except for the implanted area. The range of the implanted layer was estimated to be \(\sim 500 \text{ nm}\) for S12A7 with a TRIM code analysis.\(^{19}\) Electron
doping by replacing the free $O^{2-}$ ions with electrons was performed by a reduction treatment using an oxygen-deficient amorphous C12A7 layer, where the amorphous C12A7 layer works as an oxygen getter, removing the free $O^{2-}$ ions from the S12A7 film. The detailed procedure is described in ref. 20. The amorphous layer was removed by a mechanical polishing before electrical measurements.

Crystal structures of the films were identified by X-ray diffraction (XRD) measurements (Rigaku, RINT2500). Optical transmission spectra were measured in the UV to near infrared region (NIR) using a conventional spectrophotometer (Hitachi, U4000) at RT. Electrical conductivity measurements were carried out using a standard four-probe method. Carrier concentrations were evaluated from Hall voltage measurements using a van der Pauw configuration.

3. Results and discussion

It was confirmed that XRD patterns of as-deposited S12A7 showed only broad halos except for diffraction peaks from the substrates, substantiating that the as-deposited films were amorphous. Figure 1 shows the XRD patterns of the films after the post annealing. A calculated XRD pattern of S12A7 is also shown for identification. It is seen that all of the diffraction peaks correspond to the S12A7 phase or the substrates for both the films fabricated on the MgO and YAG substrates. Therefore, the crystalline phase of the obtained films is identified as S12A7, and the films are non-preferentially oriented polycrystalline.

Then, $H^+$-implantation and UV-light illumination were carried out for the crystallized S12A7 films. Inset to Fig. 2(a) shows optical transmission spectra of the $H^+$-implanted S12A7 film before and after the UV-light illumination, and Fig. 2(a) shows a difference spectrum for optical absorption coefficient calculated from the transmission spectra. The difference spectrum shows that extra absorption is induced at $\sim 0.4$ eV due to the UV-light illumination. Similar to the $H^+$-bearing C12A7 case, the UV-light induced absorption band at $\sim 0.4$ eV accompanies an appearance of electronic conductance also for S12A7. Figure 2(b) shows the temperature dependence of the electrical conductivity of the as-implanted and UV-light illuminated S12A7 films. The conductivities of the as-crystallized and $H^+$-implanted films were very low ($<10^{-10}$ S cm$^{-1}$, the detection limit of the apparatus). However, the UV-light illumination enhanced the conductivity largely by $\sim 7$ orders of magnitude to $\sim 1 \times 10^{-3}$ S cm$^{-1}$ at RT. The temperature dependence of the conductivity follows well an Arrhenius-type thermally-activated behavior with an activation energy of $\sim 0.15$ eV.

These optical and electronic phenomena are similar to those observed on $H^+$-bearing C12A7. Therefore, as an analogue to $H^+$-bearing C12A7, it is reasonable to consider that the electrons are photo-released from the hydride ions and the released electrons are loosely engaged in the cages to form $F^-$-like centers also in S12A7. The absorption band at $\sim 0.4$ eV is...
due to the inter-cage transition of the encaged electrons and the electrical conduction is produced by the electron migration through neighboring cages.

Next, the as-crystallized S12A7 films were subjected to the reduction treatment using an oxygen-deficient C12A7 film deposition to produce S12A7 electrode films. Figure 3(a) shows the temperature dependence of the resistivity for two S12A7 electrode films (samples A and B). RT conductivities of samples A and B are 200 and 270 S cm⁻¹, respectively. These values are larger than that of the H⁺-implanted & UV-illuminated S12A7 film. In addition, the S12A7 electrode films exhibit a metallic conduction as seen in the positive temperature coefficients of the resistivity, although the H⁺-implanted & UV-illuminated S12A7 film showed the thermally-activated conduction. Carrier concentrations obtained by the Hall voltage measurements at RT are 1.3 × 10¹⁰ cm⁻³ for sample A and 1.4 × 10¹⁰ cm⁻³ for sample B, while Hall mobilities of those films are respectively ~0.97 cm² V⁻¹ s⁻¹ and ~1.2 cm² V⁻¹ s⁻¹. For the H⁺-implanted & UV-illuminated S12A7 film, the carrier concentration was estimated from the RT conductivity upon the supposition of a drift mobility of 1 cm² V⁻¹ s⁻¹, which gives the carrier concentration of ~6 × 10¹⁰ cm⁻³, because a Hall voltage could not be measured. It is reported that C12A7 electrode exhibits an insulator-metal transition when the electron concentration exceeds ~1 × 10¹ⁱ cm⁻³ (i.e. C12A7 electrode film also exhibits a metallic conduction as shown in Fig. 3(a)). Thus, it is reasonable that the metallic conduction is observed in the S12A7 films with electron concentrations greater than 1.3 × 10¹⁰ cm⁻³. Metallic conduction in S12A7 electrode films is further confirmed by the appearance of Drude-type free carrier absorptions in infrared region in the optical absorption spectra (Fig. 3b). Moreover, two extra absorption bands at 2.45 eV and 3.5 eV are observed for the S12A7 electrode. As an analogue to C12A7 electrode (an absorption spectrum is shown for comparison), the 2.45 eV absorption is likely associated with the intra-cage s–p transition of the anionic electrons. The absorption peak shift from 2.71 eV (C12A7) to 2.45 eV (S12A7) may be due to the expansion of the cage size in S12A7. The origin of the absorption at ~3.5 eV is unclear at present. Possible candidates are transitions from the free O²⁻ ions to a cage conduction band or intra s–p transition in O²⁻ ions.

4. Summary
Thin films of polycrystalline S12A7 were fabricated by PLD and a post-annealing treatment. The proton implantation followed by the UV-light illumination and the reduction treatment doped anionic electrons in the crystallographic cages in S12A7. The as-crystallized films and the H⁺-implanted films were electrical insulator. While, a drastic increase in the conductivity from ~1 × 10⁻¹⁰ S cm⁻¹ to ~1 × 10⁻¹³ S cm⁻¹ was observed by the subsequent UV-light illumination to the H⁺-implanted films, accompanying a slight increase in the optical absorption at ~0.4 eV. Further, higher (metallic) conductive S12A7 electrode films were obtained by the reduction treatment and the conductivity reached 270 S cm⁻¹ at RT. The anionic electrons in S12A7 behave in a way similar to that in C12A7. These results indicate that S12A7, which has the same crystal structure as C12A7, provides a new platform to cultivate the electronic functions by utilizing a built-in nanoporous structure with a larger free space as well as an opportunity to engineer the properties of the thin films via the formation of solid-solution with C12A7.

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References
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14) K. Hayashi, N. Ueda, M. Hirano, T. Kamiya and H. Hosono, to be published.