Preparation of Cerium Dioxide Thin Films via Sol-Gel Process and Their Characteristics as Electrical Buffer Layers

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ゾル-ゲル法による二酸化セリウム薄膜の作製と電気的バッファ層としての特性

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CeO₂ thin films were prepared on Si(100) and Si(111) substrates from cerium acetate monohydrate via sol-gel process. The thin films were crystallized at approximately 700°C and had polycrystalline microstructure. Scanning electron microscopy (SEM) observation showed that those films consisted of small grains of 60-70 nm in diameter and had even surfaces. SrTiO₃ films with a platinum top electrode were formed on Pt/Si and Pt/CeO₂/Si substrates. Current voltage (*I-V*) characteristics of the SrTiO₃ films were measured on Pt/SrTiO₃/Pt/Si and Pt/SrTiO₃/Pt/CeO₂/Si structures. The leakage current density for the former sample was approximately 6.6×10^{-6} A/cm² under the applied electric field of 9.4×10^4 V/cm. An increase in the applied electric field above 9.4×10^4 V/cm resulted in a marked increase in the leakage current. The leakage current for the latter sample was 4.1×10^{-6} A/cm² under 2.5×10^5 V/cm. The *I-V* characteristics of the SrTiO₃ films were improved by the use of the CeO₂ film as an intermediate layer.

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1. Introduction

Cerium dioxide, CeO₂, has a fluorite structure and is an important oxide material with good mechanical, chemical and thermal stabilities. CeO₂ films have been widely used as optical coatings,¹⁾ heat mirrors,²⁾ buffer materials for epitaxial high-*T_c* superconducting oxide thin films on silicon and sapphire,^{3),4)} and insulating layers in metal-oxide-semiconductor transistors⁵⁾ and high-*T_c* superconducting field effect devices.⁶⁾ To date, CeO₂ thin films have been prepared by using rf magnetron sputtering,⁷⁾ electron beam evaporation^{8),9)} and metal-organic chemical vapor deposition methods.¹⁰⁾ However, to the authors' knowledge, there is no report on the growth of CeO₂ thin films by sol-gel process. For the increased design choices of device fabrication, it is desirable to examine various deposition techniques and substrates in order to investigate growth behavior of the thin films.

This paper reports the crystallization and structural evolution of CeO₂ thin films fabricated on Si(100) and Si(111) substrates by sol-gel process. In order to study the role of CeO₂ thin film as an intermediate layer, *I-V* characteristics of SrTiO₃ films formed on Pt/Si and Pt/CeO₂/Si were measured. The interfaces of SrTiO₃/Si and SrTiO₃/CeO₂/Si were also studied by means of Auger electron spectroscopy (AES).

2. Experimental

Cerium(III) acetate monohydrate, Ce(CH₃COO)₃·H₂O, was dissolved in acetic acid at 60°C for 30 min in flowing argon gas. One volume of 2-aminoethanol was added to four volumes of the cerium acetate solution to prevent rapid hydrolysis of cerium acetate; addition of smaller amounts of 2-aminoethanol resulted in poor stability of the solution, and addition of larger amounts of 2-aminoethanol lead to poor wettability of the solution to the Si substrates. The solution was then refluxed at 110°C for 3 h in flowing Ar gas. In this way, the starting solution containing Ce(CH₃COO)₃ of about 0.15 mol/l was prepared. The solution was then coated on Si(100) and Si(111) substrates by

spin coating at 1500 rpm for 20 s and dried in air at 200°C for each layer. In order to remove the native oxide layer of Si, the substrates were etched in 20 vol% HF solution at room temperature for 3 min prior to the coating. Films of desired thickness could be obtained by multiple coating processes. The films were then heated in air at temperatures between 600 and 900°C for 3 h. After firing, samples were examined by means of X-ray θ - 2θ diffraction (XRD) and scanning electron microscopy (SEM).

In order to study the role of the CeO₂ thin film as an intermediate layer between SrTiO₃ and Si, SrTiO₃ with Pt top electrode were formed on Pt/Si and Pt/CeO₂/Si substrates. Approximately 100-nm thick Pt electrodes were sputter deposited at 500°C in flowing Ar and O₂ gasses (Ar : O₂ = 4 : 1). The ambient pressure during sputter deposition was 0.3 Pa. SrTiO₃ was deposited on the Pt electrode by the sol-gel method using a solution which was prepared by dissolving strontium acetate 0.5 hydrate and titanium tetraisopropoxide in acetic acid and 2-methoxyethanol, respectively. These two solutions were mixed and refluxed at 110°C for 12 h in flowing N₂ gas before the deposition. The heat treatment was conducted in air at 800°C for 3 h. Typical polycrystalline SrTiO₃ patterns were obtained by XRD measurements for the samples of SrTiO₃/Pt/Si and SrTiO₃/Pt/CeO₂/Si. SrTiO₃ films of 120 and 160 nm in thickness were prepared for the electrical measurements. Pt top electrode with 0.096 cm² were sputter deposited on SrTiO₃/Pt/Si and SrTiO₃/Pt/CeO₂/Si in order to measure *I-V* characteristics of the SrTiO₃ films with Pt/SrTiO₃/Pt/Si and Pt/SrTiO₃/Pt/CeO₂/Si in both structures. Since it is well-known that 100-nm thick Pt film does not prevent counterdiffusion of SrTiO₃ and Si,¹¹⁾ AES measurements were conducted on the samples with SrTiO₃/Si and SrTiO₃/CeO₂/Si structures to study the effect of CeO₂ layer to the counterdiffusion of SrTiO₃ and Si.

3. Results and discussion

Thickness of the CeO₂ films, determined by SEM cross sectional observation, increased in proportion to the

number of coating cycles. The average increase in film thickness per each coating cycle was about 30 nm, and the thickness of the films studied was about 120 nm. Figure 1 shows the XRD patterns of the CeO_2 films on Si(100) that were heat-treated at temperatures from 700° to 900°C for 3 h. The films heated at 600°C were amorphous. The films were crystallized at approximately 700°C and had polycrystalline microstructure. The CeO_2 films formed on Si(111) were also crystallized at approximately 700°C and had polycrystalline microstructure. No difference was found in crystallographical texture or crystallization temperature between the CeO_2 films deposited on Si(100) and Si(111) substrates. The full width at half maximum (FWHM) values of 0.40, 0.27 and 0.25° were obtained from the (111) peaks of the CeO_2 films grown on Si(100) substrates at 700°, 800° and 900°C, respectively. Films with good crystallinity were obtained above 800°C. Figure 2 shows SEM micrographs of the surface and cross section of the CeO_2 films heated at 800°C for 3 h. The photographs showed that the films had even surface and consisted of small grains of 60–70 nm in diameter.

I - V characteristics of the SrTiO_3 films are shown in Fig. 3 for the samples with Pt/ SrTiO_3 /Pt/Si and Pt/ SrTiO_3 /Pt/ CeO_2 /Si structures. The leakage current density for the former sample was approximately 6.6×10^{-6} A/cm² under the applied electric field of 9.4×10^4 V/cm. An increase in applied electric field above 9.4×10^4 V/cm resulted in a marked increase in the leakage current. The thickness of the SrTiO_3 layer in the former sample was ~160 nm. When the thickness of the SrTiO_3 was less than 120 nm, the leakage current density further increased up to the order of 10^{-3} A/cm². For the latter sample, on the otherhand, the leakage current density of the SrTiO_3 film was 4.1×10^{-6} A/cm² under 2.5×10^5 V/cm, though the thickness of the SrTiO_3 film was ~120 nm. Thus the I - V characteristics of the SrTiO_3 films were thus improved by the use of the sol-gel derived CeO_2 film as an intermediate layer.

Figures 4(a) and (b) show the depth profiles of AES for the samples with SrTiO_3 /Si and SrTiO_3 / CeO_2 /Si structures, respectively. Sr was not detected in these experiments. Figure 4(a) shows that diffusion of Si into SrTiO_3 layer and diffusion of Ti and O into Si substrate occurred on the sample with SrTiO_3 /Si structure. O in SrTiO_3 decreased markedly near the interface of SrTiO_3 /Si.

Fig. 1. XRD patterns of the CeO_2 thin films formed on Si(100) at various temperatures.

Fig. 2. SEM photographs of the CeO_2 thin films formed on Si(100) at 800°C for 3 h. (a) surface, (b) cross section.

Fig. 3. Current-voltage characteristics of the SrTiO_3 films for the samples with (a) Pt/ SrTiO_3 /Pt/Si and (b) Pt/ SrTiO_3 /Pt/ CeO_2 /Si structures.

Fig. 4. AES depth profiles of (a) SrTiO₃/Si and (b) SrTiO₃/CeO₂/Si. The samples were etched by Ar⁺ beam.

Figure 4(b), on the other hand, shows that little diffusion of Si into SrTiO₃ layer and Ti into Si substrate was observed by AES measurement on the sample with CeO₂ intermediate layer. Intensity of the AES signals of oxygen was almost constant throughout the SrTiO₃ layer on the sample with the CeO₂ intermediate layer. Since an increase in the leakage current of SrTiO₃ is thought to be influenced largely by oxygen vacancies in SrTiO₃,^{12),13)} the difference in the *I*-*V* characteristics of the SrTiO₃ layers between the Pt/SrTiO₃/Pt/Si and Pt/SrTiO₃/Pt/CeO₂/Si structures might mainly result from the difference of oxygen deficiencies in SrTiO₃. The leakage current of our samples was larger than reported values for well fabricated SrTiO₃ with

~100 nm in thickness, ~10⁻⁸ A/cm²,^{13),14)} because preparation conditions of Pt electrodes and SrTiO₃ were not thoroughly investigated in the present experiments. It is, however, obvious that *I*-*V* characteristics of SrTiO₃ was improved markedly by the use of the sol-gel derived CeO₂ film as an intermediate layer between SrTiO₃ and Si.

4. Conclusions

CeO₂ thin films were prepared on Si(100) and Si(111) substrates from Ce(CH₃COO)₃·H₂O via sol-gel process. The films were crystallized approximately at 700°C and had polycrystalline microstructure. The films consisted of small grains of 60–70 nm in diameter and had even surface. The leakage current density of SrTiO₃ in Pt/SrTiO₃/Pt/Si structure was approximately 6.6 × 10⁻⁶ A/cm² under the applied electric field of 9.4 × 10⁴ V/cm. An increase in applied electric field above 9.4 × 10⁴ V/cm resulted in marked increase in the leakage current. While, the leakage current density of sample with CeO₂ intermediate layer was 4.1 × 10⁻⁶ A/cm² under 2.5 × 10⁵ V/cm. The *I*-*V* characteristics of the SrTiO₃ films were improved by the use of the sol-gel derived CeO₂ film as an intermediate layer.

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