Low temperature growth of CeO$_2$(111) layer on Si(100) using dual plasma deposition

L.P. Wang $^{a,b}$, B.Y. Tang $^{a,b}$, N. Huang $^{a}$, X.B. Tian $^{a}$, P.K. Chu $^{a,*}$

$^{a}$ Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong

$^{b}$ Advanced Welding Production and Technology National Key Laboratory, Harbin Institute of Technology, Harbin, People’s Republic of China

Received 3 October 2000; received in revised form 18 November 2000

Abstract

In order to lower the growth temperature and improve the crystalline quality, the temperature effects on the growth of CeO$_2$(111) layer on Si(100) using dual plasma deposition are investigated. The as-deposited films are characterized by X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and atomic force microscopy (AFM). The XRD results show CeO$_2$(111) has been successfully deposited on Si(100) even at 200°C, and the best crystalline quality is found in the film deposited at 500°C. The CeO$_2$(111) pole figure acquired from the sample deposited at 500°C shows that the film has a strong preferred orientation. The RBS results show that the concentration ratio of Ce and O approaches the normal chemical stoichiometry as the temperature is increased. The surface topography of the films revealed by AFM discloses that as the growth temperature is increased, the surface is less rough and the density of the islands becomes higher. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cerium dioxide; Dual plasma deposition; Temperature

1. Introduction

Cerium dioxide (CeO$_2$) possesses a cubic fluorite crystal structure ($a = 5.411$ Å) and many favorable properties. It is a promising insulating material with many potential applications in microelectronics and has attracted much attention in recent years [1–8]. Owing to the small lattice mismatch and similar thermal expansion coefficient, it can be used as a protective buffer layer in high-temperature superconductors in current-carrying applications [1]. In addition, due to its relatively large permittivity (nearly 26) and high chemical stability, it can be used as an insulating layer in multilayer electronic devices such as the diffusion barrier layer between interconnects and substrates [2]. Several growth techniques have been proposed, including molecular beam epitaxy [3], pulsed laser deposition [4,5], sputtering [6], electron beam evaporation [7], and metal-organic chemical vapor deposition [1,8]. A common condition in all these fabrication techniques is that a relative high growth temperature (500–800°C) is required. Unfortunately, low-temperature film growth is required in the fabrication of multilayer electronic devices. Efforts have been made to decrease the growth temperature, but the results so far have been mediocre [7].

Dual plasma deposition [9], which is derived from plasma immersion ion implantation and deposition [10–15], has many advantages as a thin film synthesis technique. The obvious one is that a film composed of several elements, gaseous and/or metallic, with various compositions can be fabricated in the same instrument without breaking vacuum. In addition, since a metal vacuum arc plasma source is normally operated in a pulse mode, the ion density is high thereby inducing a high nucleation density on the surface. At the same time, the adatoms have a long time to diffuse and relax between the metal plasma pulses. Since the substrate is immersed in the plasma, large area uniform deposition can be achieved relatively easily as well. Last but not least, because the kinetic energy of the impacting ions can be controlled in situ by varying the voltage on the
samples, it is possible to fabricate good quality thin films at a relatively low temperature. In this paper, we investigate the temperature dependence of CeO$_2$(1 0 0) thin film growth on Si(1 0 0) by dual plasma deposition.

2. Experimental

Pieces of p-type silicon (1 0 0) 20 × 10 mm were ultrasonically cleaned in acetone, rinsed in deionized water, and dried by nitrogen. The cleaning process did not remove the oxide layer on the silicon substrate. After loading the substrates into the multi-purpose plasma immersion ion implanter [16], the vacuum chamber was evacuated to a base pressure of $5.0 \times 10^{-6}$ Torr. Cerium and oxygen plasma was generated simultaneously in the vacuum chamber by a metal vacuum arc plasma source and radio frequency (RF) source, respectively. During deposition, the flow of the oxygen gas was set to 16 sccm and the pressure in the vacuum chamber was $3.0 \times 10^{-4}$ Torr. The power of the RF source was 500 W, and the reflective power was adjusted to zero. The frequency of the metal vacuum arc plasma source was 40 Hz, and its pulse width was about 250 $\mu$s. In order to avoid breakdown of the deposited film due to charging, no bias was applied to the substrate, and so the kinetic energy of the incident metal ions was equal to its initial energy (nearly equal to 50 eV). The growth rate of CeO$_2$ film was nearly 0.1 nm/s, and the deposition time was 1 h. The substrate temperature was varied from 200 to 500°C. A cerium seed layer several nm thick was first deposited using only the Ce plasma. Subsequently, oxygen was introduced into the chamber and the oxygen plasma was generated using RF glow discharge to oxidize the Ce seed layer. Afterwards, the CeO$_2$ film was deposited in the presence of both the cerium and oxygen plasmas. To reveal the properties, the samples were characterized by X-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), and atomic force microscopy (AFM).

3. Results and discussion

Fig. 1 depicts the $\theta$–$2\theta$ XRD results of the as-deposited films. The CeO$_2$(1 1 1) peak can be observed in all of the XRD patterns, but some other peaks such as CeO$_2$(3 1 1) can only be observed in samples deposited at lower temperature. When the deposition temperature reaches 500°C, CeO$_2$(1 1 1) peak is very prominent and other peaks except CeO$_2$(2 2 2) become less salient. Moreover, when the deposition temperature goes up, the diffraction peak becomes more intense. As the thickness of the deposited film in all the samples is nearly the same, the sample exhibiting a higher CeO$_2$(1 1 1) peak should have better crystalline properties.

X-ray pole figures were obtained to investigate the in-plane texture information of the reflection plane of the as-deposited film. Fig. 2 is the (1 1 1) pole figure acquired on the surface of the sample deposited at 500°C showing that the CeO$_2$(1 1 1) peak appears only when the incident X-ray and the normal of the surface is on the same plane. As a result, our results indicate that the CeO$_2$ film deposited at 500°C has a strong preferred orientation.
Fig. 3 displays the 2 MeV He RBS spectra taken from samples deposited at different temperature at an incident angle of 7° and scattering angle of 170°. The Ce to O atomic ratios determined from the random spectra are depicted in Table 1. It can be observed that there exists excessive oxygen in the samples deposited at lower temperature, but as the temperature is increased, the Ce/O ratio approaches the normal chemical stoichiometry. All samples show uniform Ce and O concentrations through the film indicating the effectiveness of the dual plasma deposition process.

The surface topography of the films is investigated by AFM and the images are depicted in Fig. 4. The scanned area is $4 \times 4 \, \mu m^2$. Here, we use the measured peak height to indicate the surface roughness. As shown in the AFM images, when the deposition temperature goes up, the islands density increases and the surface toughness decreases.

In our experiments, we intentionally did not remove the native oxide on the silicon substrate, and so the silicon crystal orientation should have little effects on the CeO$_2$ film deposition. Since the (1 1 1) plane has the lowest energy during nucleation on the SiO$_2$ surface, a strong CeO$_2$(1 1 1) peak is observed in the XRD patterns. In addition, when the temperature goes up, diffusion of the adatoms is enhanced, and the cerium atoms can more effectively bond with oxygen atoms to make the crystal quality better. At the same time, as the deposition temperature is increased, corner diffusion and island diffusion are enhanced also [17]. Hence, the surface roughness diminishes.

4. Conclusion

CeO$_2$ films have been grown on Si(1 0 0) substrates by dual plasma deposition at different temperature. The XRD results show that all the as-deposited films have a (1 1 1) preferred orientation, and when the temperature is higher, the intensity of the CeO$_2$(1 1 1) peak is higher. The (1 1 1) pole figure shows that the CeO$_2$(1 1 1) peak can only be found when the incident X-ray and the normal of the surface are located on the same plane. RBS data convey that as the temperature is increased, the atomic ratio of Ce to O gradually approaches the normal chemical stoichiometry, and all the samples have uniform Ce and O concentrations throughout the thickness of the films. The AFM images show that surface roughness decreases and the island density increases as the growth temperature goes up.

Acknowledgements

This work described in this paper was jointly supported by grants from the Hong Kong Research Grants

<table>
<thead>
<tr>
<th>Temperature during deposition</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic concentration ratio</td>
<td>1:2.47</td>
<td>1:2.29</td>
<td>1:2.25</td>
<td>1:2.12</td>
</tr>
</tbody>
</table>
Fig. 4. AFM surface topography of the as-deposited films.

References