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Growth of HfO_2 films using an alternate reaction of $HfCl_4$ and O_2 under atmospheric pressure

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Abstract

HfO_2 films were deposited onto a Si(1 0 0) substrate using an alternate reaction of $HfCl_4$ and O_2 under atmospheric pressure. Self-limiting growth of the HfO_2 was achieved in the range of the growth temperature above 873 K. The X-ray diffraction of the HfO_2 films showed a typical diffraction pattern assigned to the monoclinic polycrystalline phase. Residual chloride concentration in HfO_2 films were not higher than 0.1 at%. When the growth temperature was 973 K, the $HfSiO_x$ is formed in HfO_2 film. This gives effective permittivity value of 9.6 for the HfO_2 film grown at 573 K.

Keywords: HfO_2; Film; Atmospheric pressure; Self-limiting growth; Permittivity value

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1. Introduction

Hafnium dioxide is a dielectric materials with a wide band gap [1,2], relatively high refractive index [1,3] and high thermal stability [4]. For these reasons HfO_2 has found applications in optical coating [5,6], in particular, when high optical damage thresholds are needed [7]. In addition, HfO_2 is effective as a buffer layer. In the last few years, however, the main interest in HfO_2 is related to further development of microelectronic devices for practical applications such as strong capacitor and gate insulators, the films should be grown with accurately controlled thickness and with a smooth surface. An interesting method for depositing thin films is atomic layer deposition (ALD). ALD is a pulsed technique in which the growth takes place from alternately and separately supplied gaseous sources through self-limiting surface reactions [8]. If self-limitation is realized the films will be uniform over large areas and have a thickness that is proportional to the number of completed deposition cycles.

All the ALD methods being applied for the preparation of metal oxides so far have been studied under reduced pressure. However, the preparation under reduced pressure tends to form oxygen defects. This is not appropriate for the purpose described above. In a previous paper, we reported that ZnO and ZrO_2 films are successfully grown by an alternate reaction of sources under atmospheric pressure (AP-ALD) [9–12]. In this report, we describe the results of the investigation on the growth of HfO_2 layers under atmospheric pressure, using the alternate reaction of $HfCl_4$ adsorption onto a Si(1 0 0) substrate and its oxidation. Since no hydrogen containing species are involved in this process, it should be possible to reduce the quality of the films and the stability of HfO_2-based metal–oxide–semiconductor devices.

2. Experimental

$HfCl_4$ (98%) and O_2 (99.995%) gas were used as the Hf and O sources, respectively. Films of HfO_2 were deposited onto a Si(1 0 0) substrate (10 mm × 10 mm) using a horizontal quartz hot-wall type ALD reactor, as

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shown in Fig. 1. $HfCl_4$ was evaporated at 433 K and introduced into the growth zone with purified N_2 as a carrier gas. Oxidation was carried out using O_2, which was introduced into the deposition zone with purified N_2 as well. To prevent the source materials from mixing with each other, they were separated by a purified N_2 gas flowing curtain in the middle of the reactor. The Si(1 0 0) substrate was mounted on the quartz rod. Gaseous $HfCl_4$ and O_2 were supplied alternately to the substrate by moving the rod back and forth automatically with a computer-controlled system. The gas flow sequence of the growth per cycle consists of four steps as follows: supply $HfCl_4$ for 5 s (step 1), purge with N_2 for 10 s (step 2), supply O_2 for 10 s (step 3), and then purge with N_2 for 10 s (step 4). A, B, C, and D in Fig. 1 stand for the positions of the substrate corresponding to the steps 1–4, respectively. This cycle was repeated 10–500 times. The typical growth conditions are summarized in Table 1.

Crystallographic structure of the deposited films was examined by a Rigaku RINT 2000 X-ray diffractometer (XRD). The film thickness was evaluated by high-resolution scanning electron microscopy (HR-SEM). The X-ray photoelectron spectroscopy (XPS) spectra were measured using a Shimadzu XRTOS-XSAM 800 X-ray photoelectron spectrometer. Transmission electron microscopy (TEM) was applied for selected samples to examine the interface layers between HfO_2 and silicon. The secondary ion mass spectroscopy (SIMS) spectra were measured using HITACHI PHI-6650 Q-pole SIMS. The electrical properties were measured by C–V (capacitance–voltage).

3. Results and discussion

Fig. 2 shows XRD patterns of HfO_2 films in the 500 cycles growth deposited at (a) 573 K, (b) 773 K and (c) 973 K, respectively. Thickness of HfO_2 films grown at 573, 773 and 973 K were 89, 119 and 130 nm, respectively. It is apparent that the diffraction peaks appearing at 28.3° and 31.6° are assigned to the $(\bar{1}\,1\,1)$ and (1 1 1) diffractions of HfO_2 with a monoclinic phase. Therefore, trace reflection from orthorhombic phase is also detected at a 2θ value of 30.4°, as shown in Fig. 2(b). This is characteristic of HfO_2 since similar minor reflections from metastable phases are also seen in the films [13–16]. However, Fig. 2(a) did not appear a monoclinic phase at 573 K, where the temperature is obviously too low to initiate noticeable crystallization.

Table 1
Typical growth conditions

Substrate	Si(1 0 0)
Growth temperature	523–923 K
$HfCl_4$ partial pressure	12.7 Pa
O_2 partial pressure	2.7×10^4 Pa
Total gas flow rate	$1.0 \times 10^{-5}\,m^3\,s^{-1}$
Time sequence	5 s–10 s–10 s–10 s

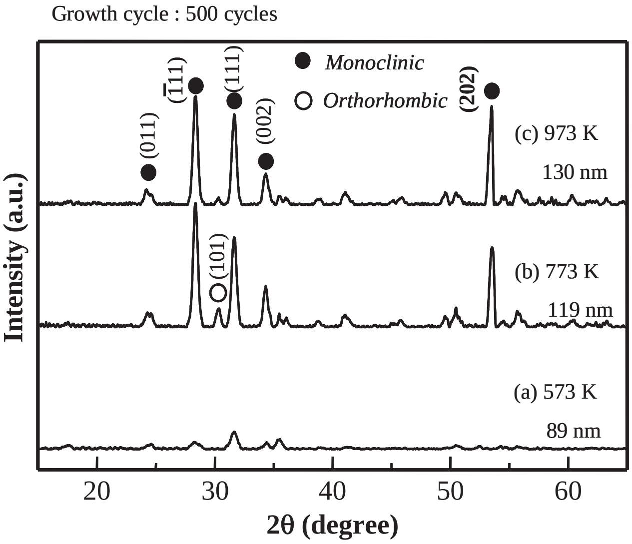

Fig. 2. XRD patterns of the HfO_2 films deposited on Si(1 0 0) at (a) 573 K, (b) 773 K and (c) 973 K.

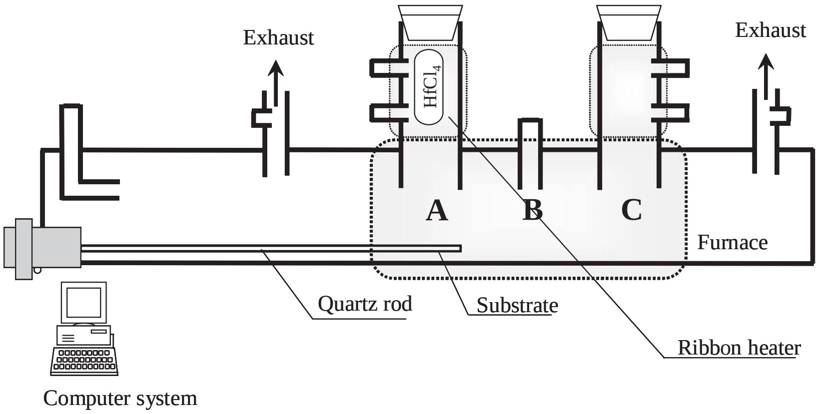

Fig. 1. Schematic diagram of the AP-ALD system.

One of the notable features of the ALD method is that the film thickness is controlled only by the number of growth cycles. Fig. 3 shows the plot of the HfO_2 film thickness as a function of the growth cycle. As is shown in Fig. 3, it is obvious that the HfO_2 film thickness increases linearly with the number of cycles. From the slope of the obtained straight line in Fig. 3 the stepwise growth per cycle is estimated to be 0.26 nm. This suggests that the ALD growth of the HfO_2 film is governed by the self-limiting adsorption reaction of $HfCl_4$ onto the Si substrate.

Fig. 4 shows the growth rate of the HfO_2 films as a function of the growth temperature. The growth rates are independent of the temperature in the range above 873 K. As a result, it is obvious that the self-limiting growth of HfO_2 is completed for growth temperature above 873 K. On the other hand, in the temperature range below 873 K, the growth rate decreases with the declining substrate temperature. This is because film structure changes when the growth temperature is below 873 K.

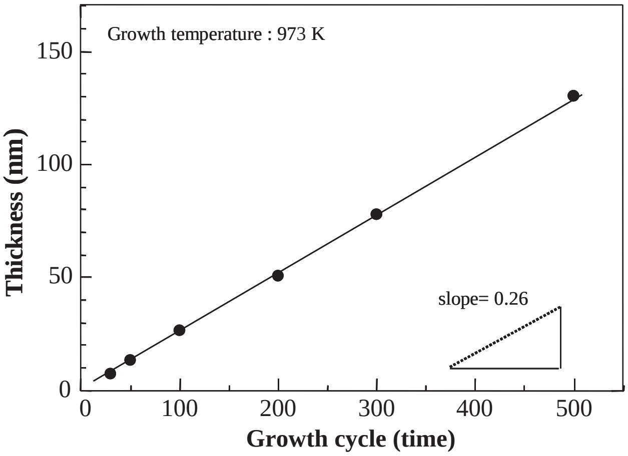

Fig. 3. Relationship between growth thickness and growth cycle at 973 K.

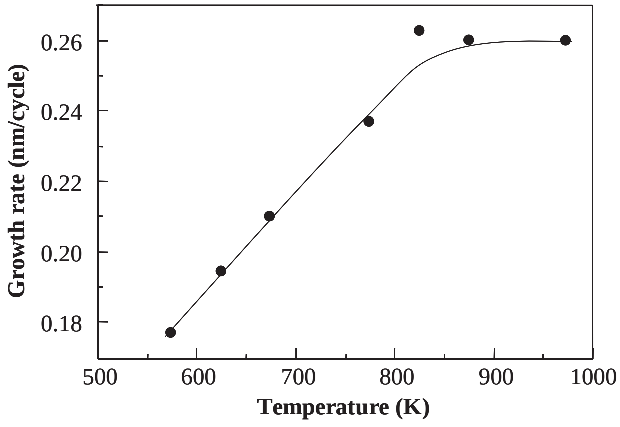

Fig. 4. Growth rate of HfO_2 films as a function of growth temperature.

Fig. 5 shows the TEM cross sectional image of the HfO_2 film at 573 K. TEM demonstrated that an amorphous SiO_2 layer of approximately 2.7 nm in thickness is formed at the substrate-film interface, as shown in Fig. 5. Similarly, all film existed about 2.5–3.0 nm interface layers between HfO_2 film and Si substrate. Therefore, when the growth temperature is 573 K, most of the film is amorphous and a part of the film crystallizes. This is in agreement with a XRD result, as shown in Fig. 2(a).

Fig. 6 shows the representative XPS spectra of the as-deposited HfO_2 film at 573 K. Film thickness is about 90 nm. It is seen that the peaks assigned to Hf(4$f_{5/2}$), Hf(4$f_{7/2}$) and O(1S) appear at binding energies of 18.6, 17.0 and 530.2 eV, respectively. The Hf(4$f_{7/2}$) peak position agrees with the reported binding energy of 17.0 eV for HfO_2 [15]. Also, any peaks assigned to chloride were not observed, implying that there is little contamination of this element. Similarly, chloride spectra could not be observed, when the growth temperature is 773 and 973 K.

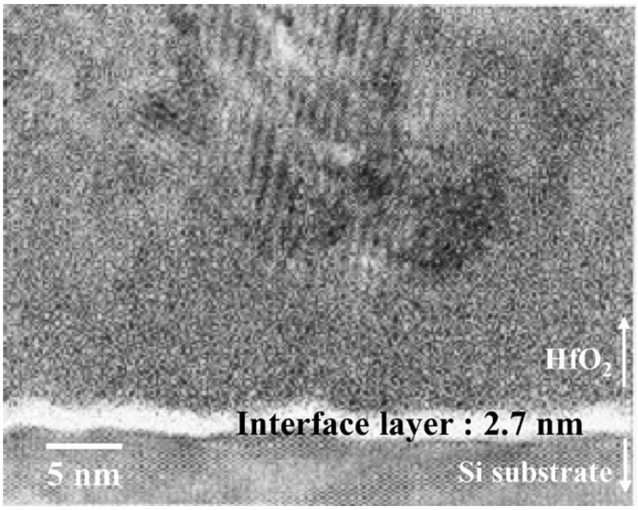

Fig. 5. TEM cross sectional image of the HfO_2 film deposited at 573 K.

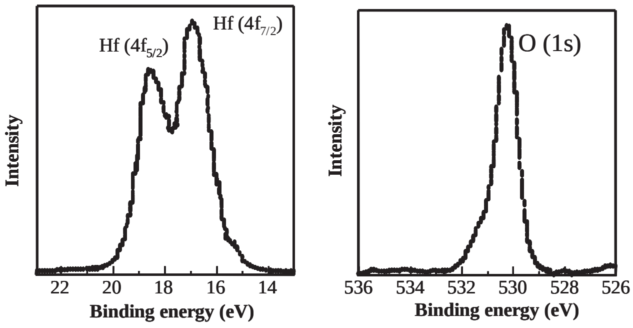

Fig. 6. XPS spectra of HfO_2 HfO_2 film deposited at 573 K.

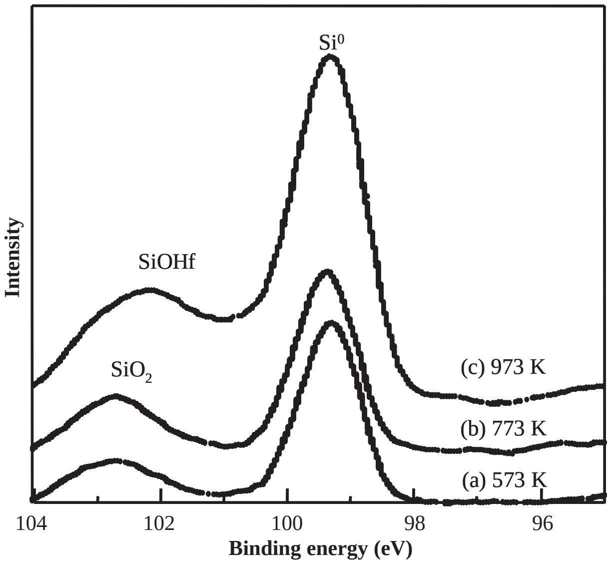

Fig. 7. XPS spectra of the ultra thin HfO_2 film deposited on Si(1 0 0) at (a) 573 K, (b) 773 K and (c) 973 K.

In order to consider the chemical bond state of an interface, XPS measures ultra thin HfO_2 films. Fig. 7 shows the XPS Si 2*p* spectra of the Ar^+ sputtering HfO_2 films at (a) 573 K, (b) 773 K and, (c) 973 K. Film thickness are about 1.8, 2.4 and 2.6 nm, respectively. The signature of these groups can be seen from the Si 2*p* spectrum, consisting of a large contribution of the Si substrate at 99.2 eV, and a smaller one to higher BE related to the intermediate SiO_2 layer. This latter contribution exhibit four secondary features, the one with the highest chemical shift with respect to Si (+3.8 eV) corresponding to fully oxidized Si (SiO_2). However, the different spectrum appears between Si and SiO_2 spectrum, when the growth temperature is 973 K. This spectrum implies the Hf silicate ($HfSiO_x$) [17,18]. This $HfSiO_x$ is related to diffusion of silicon, since it is a reaction under high temperature.

Fig. 8 shows SIMS profiles (positive ion measurement) (secondary ion intensity vs. depth) on Si(1 0 0) substrate with interface layer at (a) 573 K, (b) 773 K, and (c) 973 K, respectively. At the temperature of 573 K, signals from chloride residues are observed between HfO_2 film and Si(1 0 0) substrate. However, chloride signal was not observed by XPS spectra. Therefore, chloride concentration is not higher than 0.1 at%. And, chloride ion intensity decreases as the growth temperature is raised. And, a part of silicon (from Si substrate) has diffused into HfO_2 film at 973 K. As a result, the $HfSiO_x$ is formed in HfO_2 film (near the interface layer) by XPS spectra and SIMS profile at 973 K.

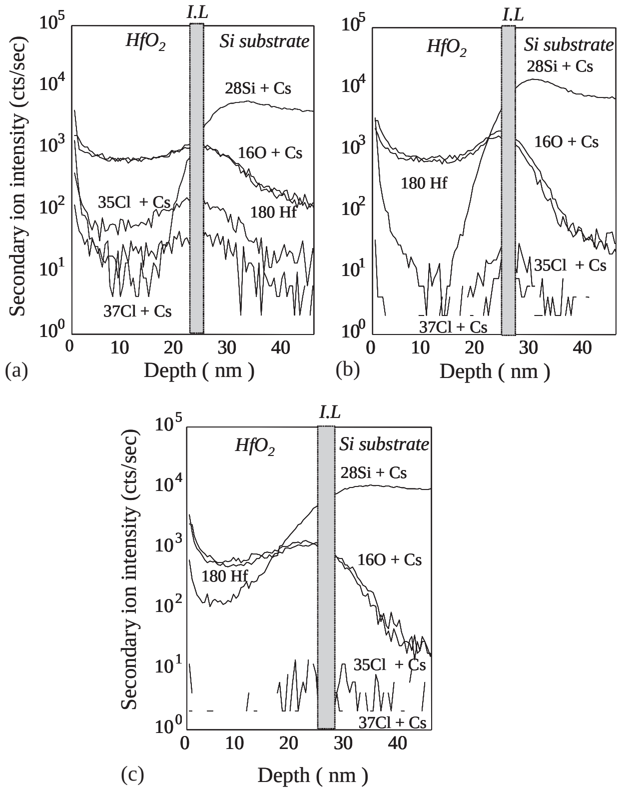

Fig. 8. SIMS depth profiles for HfO_2 films deposited on Si(1 0 0) at (a) 573 K, (b) 773 K and (c) 973 K.

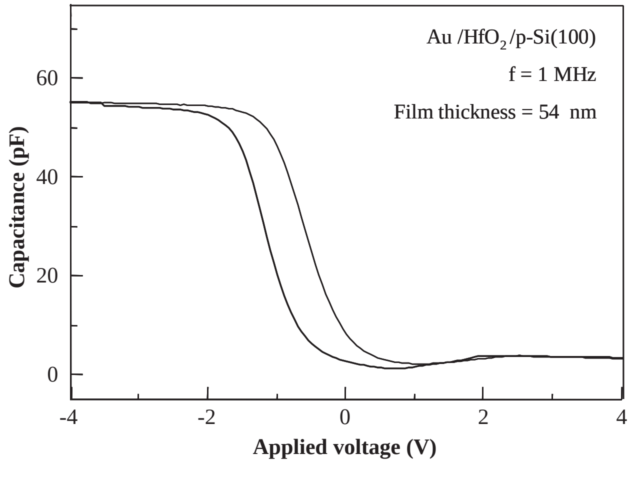

Fig. 9. Capacitance–voltage curve measured on $Au/HfO_2/Si(1 0 0)$ capacitors at 1 MHz.

Fig. 9 shows *C–V* curve measured at 1 MHz for a $Au/HfO_2/Si(1 0 0)$ structure. HfO_2 film was deposited at 573 K. Film thickness is about 54 nm. The *C–V* curve exhibits clear accumulation under strongly negative bias voltage. The effective permittivity of the dielectric oxide layer(s) can be calculated from the accumulation capacitance by using the simple parallel plate capacitor model. This gives effective permittivity values of 9.6 for the HfO_2 film growth at 573 K. And, the effective permittivity value of 8.2, and 8.5 for the HfO_2 films at 773, and 973 K, respectively. The difference of permittivity value at growth temperature is related to the crystallinity of HfO_2 film, as shown in Fig. 2. In this study, the poor crystallinity HfO_2 film growth at 573 K showed the high permittivity value. And, it is easy to produce a defect in HfO_2 film result from metastable phase at 773 K. Therefore, this result of low permittivity values result from the diffuse silicon ($HfSiO_x$), when the growth temperature is at 973 K.

4. Conclusions

In conclusion, the HfO_2 film has been successfully grown on a Si(1 0 0) substrate by means of the ALD technique using the alternate reaction of $HfCl_4$ and O_2 under atmospheric pressure. It was suggested that the AP-ALD growth was governed by the self-limiting adsorption reaction of $HfCl_4$. Crystal structure of HfO_2 film is strongly dependent on the growth temperature. There is little contamination of the chloride in HfO_2 film. And, a part of silicon (from Si substrate) had diffused into HfO_2 film at 973 K. The effective permittivity values of HfO_2 film grown at 573 K is 9.6.

Acknowledgments

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