Optical properties of a HfO_2/Si stack with a trace amount of nitrogen incorporation*

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Abstract: HfO_2 films were deposited by atomic layer deposition through alternating pulsing of $Hf[N(C_2H_5)(CH_3)]_4$ and H_2O_2. A trace amount of nitrogen was incorporated into the HfO_2 through ammonia annealing. The composition, the interface stability of the HfO_2/Si stack and the optical properties of the annealed films were analyzed to investigate the property evolution of HfO_2 during thermal treatment. With a nitrogen concentration increase from 1.41 to 7.45%, the bandgap of the films decreased from 5.82 to 4.94 eV.

Key words: atomic layer deposition; HfO_2; rapid thermal annealing; optical property

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1. Introduction

One of the bottlenecks to the further scale-down of CMOS devices is the limitation of gate tunneling leakage. According to scaling theory, when the device channel length L is scaled down, the gate oxide thickness t_{ox} should be scaled down proportionally, when the dimension of the semiconductor device is less than 50 nm and the equivalent thickness of the gate oxide layer is less than 1.3 nm. SiO_2 faces a formidable challenge in further scale reduction because it will soon arrive at the fundamental limit, which originates from quantum tunneling phenomena[1, 2]. One way to solve this problem is to use a high-k dielectric, which will allow an increased physical thickness to improve device performance. In order to fulfill the requirement of CMOS devices, high-k gate dielectrics should present several superior electronic and physical properties, such as the energy barrier between metal/oxide and Si/oxide, which should be high enough to suppress the electron inject from the metal gate and silicon[3], good thermal stability and high crystallization temperature. At present, among all the high-k dielectrics, HfO_2 has a high k value (about 25), a wide bandgap (5.7 eV), a large conduction band offset ΔE_c (1.5 eV) and valence band offset ΔE_v (3.4 eV) to Si, good thermodynamic stability and good lattice matching characteristics with Si. As a result, HfO_2 is the most widely studied and widely used high-k dielectric.

Proper nitrogen incorporation into gate dielectric films has been investigated with a variety of methods in order to provide films with a lower gate leakage current, improved interface properties and suppressed boron penetration[4–7]. Despite there are being a lot of research dedicated to HfO_2 with incorporated nitrogen, only a small number of reports focusing on its optical properties have been published so far. In this study, the optical property evolution of atomic layer deposited HfO_2 treated in NH_3 atmosphere by rapid thermal annealing (RTA) was investigated through spectroscopic ellipsometry (SE). We found that the bandgap energy of N-doped HfO_2 decreases with an increase in annealing temperature from 5.82 to 4.94 eV. In addition, the chemical composition of the film and interface property of the HfO_2/Si stack was also investigated as a function of annealing temperature.

2. Experiment

The HfO_2 film was grown by atomic layer deposition on a p-type Si (100) wafer. Prior to deposition, a p-type Si (100) wafer with a resistivity of 8–10 Ω·cm was cleaned using a standard Radio Corporation of America method, and then dipped in a 2% HF solution to remove the native oxide. $Hf[N(C_2H_5)(CH_3)]_4$ (TEMAH) and H_2O_2 were chosen as the metal source and oxidant, respectively, and the growth temperature was set to 300 ℃. The as-prepared HfO_2 films were then subjected to RTA, with the temperature up to 600, 800 and 1000 ℃ in NH_3 ambient for 30 s. The thickness and bandgap of the films was measured by SE. The thickness of the films is fitted to be 8.0 nm for as-deposited samples, and after annealing it shrinks to 7.49, 7.77 and 7.93 nm because of thermal densification. Our SE equipment (SOPRA 5E) used an Xe lamp as the light source to acquire spectra in the visible-UV range from 0.56 to 6.53 eV, with an 0.01 eV step. All the SE results were obtained at an incidence angle of 75°. Tauc-Lorentz dispersion law function was used to fit the obtained experimental data, and the chemical bonding states of the films were obtained from X-ray photoelectron spectroscopy (XPS) with an MgKα ($h\nu = 1253.6$ eV) radiation source. The binding energies of the core levels are calibrated against an adventitious C1s peak (285.0 eV) in this case.

3. Results and discussion

Figure 1 shows the N1s spectra as a function of anneal-

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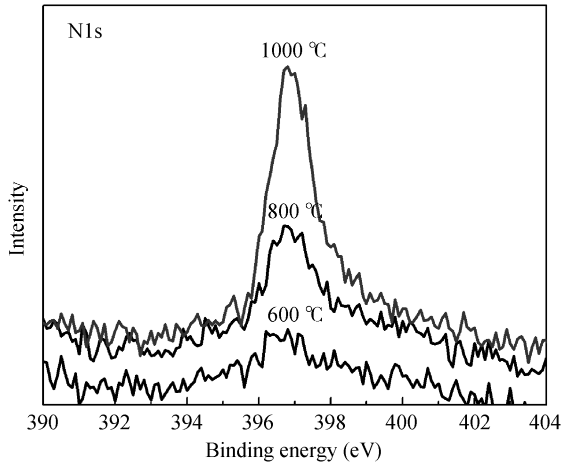

Fig. 1. XPS spectra of N1s for HfO_2 films at annealing temperatures from 600 to 1000 ℃ in NH_3 atmosphere.

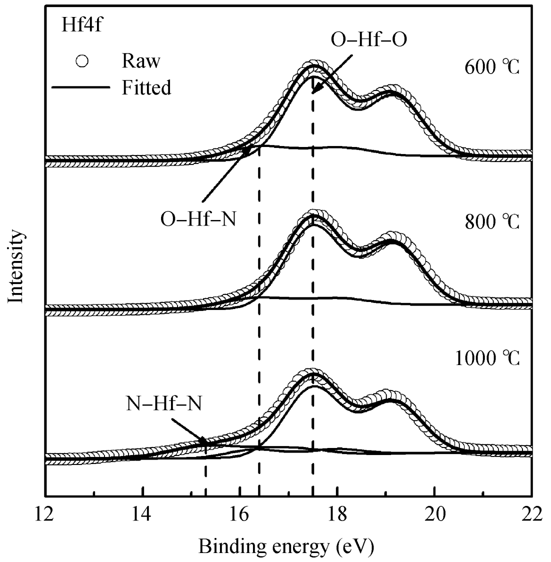

Fig. 2. The Hf4f spectra for the HfO_2 film after annealing at temperatures from 600 to 1000 ℃ in the NH_3 atmosphere.

ing temperature in NH_3 atmosphere. As shown in Fig. 1, it is clear that the nitrogen is incorporated into the HfO_2 films with the binding energy at 396.2 eV[8]. The total amount of nitrogen increases with an increase in annealing temperature, which is consistent with previous reports[9]. The Hf4f photoelectron spectra for the HfO_2 film, after annealing with the temperature from 600 to 1000 ℃ in the NH_3 atmosphere, are shown in Fig. 2. Hf4f core level spectra were deconvoluted with Gaussian-Lorentzian functions into two pairs of sub peaks. The separation between the $Hf4f_{5/2}$ and $Hf4f_{7/2}$ peaks is fixed to be 1.66 eV. The Hf4f signal of the 600 ℃ annealing sample shows two distinguished peaks: one located at 16.4 eV and the other at 17.5 eV, which is attributed to O–Hf–O bonding states. The peak at 16.4 eV corresponds to O–Hf–N bonding states and shows a small shift towards the lower binding energy with increasing annealing temperature, and there is another peak located at 15.3 eV at 1000 ℃ which is because more and more N is incorporated into the film so that the N–Hf–N bond generates. This is consistent with the fact that Pauling's electronegativity of O is larger than that of N, and as a result will induce Hf4f core level in N-doped HfO_2 shifts to lower energy with increasing N concentration.

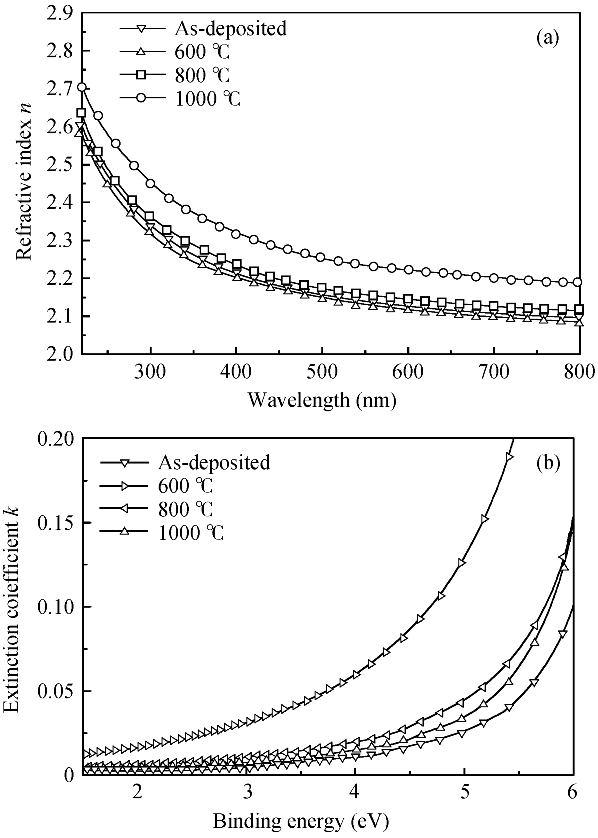

Fig. 3. (a) Refractive index, n, and (b) extinction coefficient, k, as a function of wavelength for the as-deposited and annealed samples.

Figure 3(a) shows the refractive index, n, deduced from the analysis of the SE results as a function of wavelength for the as-deposited and annealed films in NH_3 atmosphere. The refractive index of the as-deposited HfO_2 film at the 632.8 nm wavelength is 2.12. In addition, the refractive indexes of the samples annealed at 600, 800 and 1000 ℃ at 632.8 nm are up to 2.11, 2.14 and 2.21, respectively. The as-deposited film, which was deposited at a lower temperature, has a less packed structure. RTA treatments facilitate the mobility of the atoms or molecules of the films, resulting in packed films with dense atomic packing and structural ordering. The compactness of the films will induce a decrease in the n value and a decrease in film thickness. On the other hand, since the amount of incorporated N increases with the annealing temperature, and the refractive index of the Hf_3N_4 is as high as 2.3–2.4, it is easy to understand that the refractive indexes of the films would increase.

Figure 3(b) illustrates the extinction coefficient (k) of the films. Based on the extinction coefficient of these films, the optical bandgap can be obtained with the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \qquad (1)$$

where $h\nu$ is the photon energy, λ is the wavelength of the incident light, and α is the absorption coefficient which can be obtained by the equation $\alpha = 4\pi k/\lambda$. In Fig. 4, the tangent

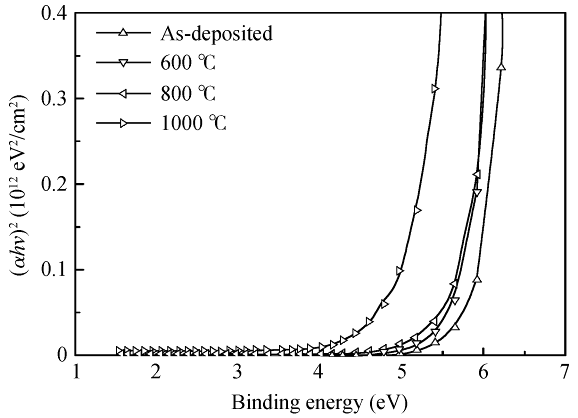

Fig. 4. Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the determination of optical bandgaps.

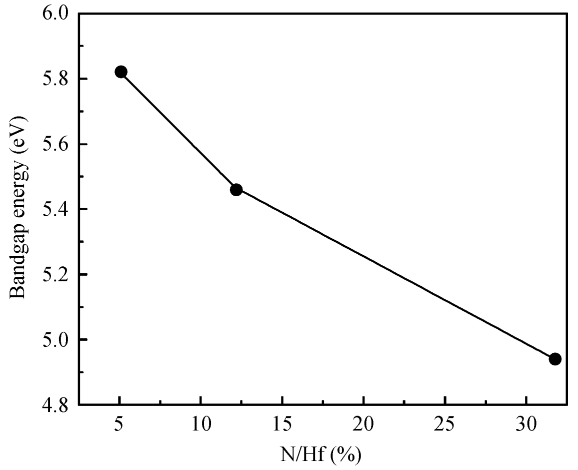

Fig. 5. Relationship between bandgap energy, E_g, and the proportion of N/Hf in the films.

of the curve crosses with the x-axis; the cross point is considered as the estimated optical bandgap. The extracted optical bandgap results are shown in Fig. 4, and the extracted E_g^{opt} for the as-deposited sample is 5.58 eV. This is consistent with the previous reports that the bandgap of HfO_2 is in the range 5.2–6.0 eV[11, 12]. The extracted E_g^{opt} value for the 600 ℃ annealing sample is 5.82 eV, which is higher than the as-deposited sample because of thermal densification. When the annealing temperature of the samples is further increased to 800 ℃, the bandgap is reduced to 5.46 eV since a significant amount of N is incorporated into the film according to XPS analysis. Moreover, a large reduction is observed after annealing at 1000 ℃, and the extracted optical bandgap is only 4.94 eV. Along with the XPS analysis, we speculate that the N–Hf–N contributes to the reduction in bandgap, since the bandgap of Hf_3N_4 is only 1.8 eV, which is smaller than HfO_2[13]. The relationship between bandgap energy and the proportion of N/Hf in films is summarized in Fig. 5. The bandgap energy decreases as nitrogen concentration increases, and it decreases abruptly at certain nitrogen concentration, depending on annealing temperature.

4. Conclusion

In summary, the influence of annealing temperature in NH_3 on the optical properties of HfO_2 films was investigated by SE. Analysis of the ellipsometric spectra indicates that the injection of N can greatly affect the refractive index and the optical bandgap of HfO_2 films. This can be attributed to N–Hf–N generation with high annealing temperature. These observations give helpful insights into the fabrication of advanced CMOS devices with high-k gate dielectrics.

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