High-k Gate Dielectric Films Studied by Extremely Asymmetric X-ray Diffraction and X-ray Photoelectron Spectroscopy

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Abstract. We studied HfAlO x(N)/SiO2/Si films which were fabricated by the layer-by-layer deposition and annealing (LL-D&A) method with different annealing conditions. In this time, in-situ annealing was performed at various temperatures in an NH3 ambient. In addition, post-deposition annealing (PDA) was performed for some samples. For each sample, the interfacial lattice strain was evaluated using extremely asymmetric X-ray diffraction and the local dielectric constant near the Al atoms was measured by X-ray photoelectron spectroscopy (XPS). Observation of the strain field was done by measuring the X-ray rocking curve of the Si 113 reflection of the Si (001) substrate under grazing incidence conditions. It was found that in the case of the samples without PDA, for higher in-situ annealing temperatures compressive strain is introduced and the local dielectric constant becomes lower. For the samples with PDA, the differences of the lattice strain and the local dielectric constant are small for different in-situ annealing temperatures.

1. Introduction

High-k films are anticipated to be used as gate insulator films for next-generation semiconductor integrated circuits. However, when a high-k film is grown, lattice strain is observed in the substrate near the interface [1]. The strain can cause a decrease in the mobility of carriers and the reliability of the devices. To control the lattice strain, an evaluation of the lattice strain at the interface is needed. In this research, the lattice strain of HfAlO x(N)/SiO2/Si was evaluated by extremely asymmetric X-ray diffraction using synchrotron radiation. The X-ray optics of this diffraction is shown in Fig. 1. It is an extremely asymmetric Bragg-case optics under grazing incidence conditions. In this optics, the lattice strain near the crystal surface affects the rocking curve because the X-ray penetration can be limited to the crystal surface by using a glancing angle smaller than the critical angle of total reflection [1]. Furthermore, the local dielectric constant was measured with X-ray photoelectron spectroscopy (XPS). The local dielectric constant was evaluated in terms of the modified Auger parameter of Al atoms $\alpha'$. It is defined as the sum of the binding energy of the photoelectrons and the kinetic energy of the Auger electrons [2]. A shift in the value of $\alpha'$ is twice that in the relaxation energy, and it reflects the change in the dielectric constant [3].
2. Experimental

2.1. Sample
A HfAlO$_x$(N) film was grown on a Si(001) substrate by a layer-by-layer deposition and annealing (LL-D&A) process [4]. A 0.8 nm thick-HfAlO$_x$ film was deposited by atomic layer deposition (ALD) and then in-situ annealed at 750°C, 850°C or 950°C in an NH$_3$ ambient. This process was repeated 5 times to obtain a thickness of 4 nm. In addition, post-deposition annealing (PDA) was carried out for some samples at a substrate temperature of 850°C in an O$_2$ ambient.

2.2. Evaluation of the lattice strain by asymmetric extremely X-ray diffraction
Observation of the strain field was done by measuring the X-ray rocking curve of the Si 113 reflection of the Si (001) substrate under grazing incidence conditions at room temperature and atmospheric pressure at beamline 15C, Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. We calculated the integrated logarithmic intensities of the measured rocking curves. The slope of the integrated intensity versus X-ray wavelength curve reflects the strain field near the crystal surface because the dependence of the integrated intensity on the X-ray wavelength is sensitive to the strain field, but the effect of absorption by the overlayer can be ignored due to taking the logarithm [5].

2.3. Measurement of the local dielectric constant by XPS
The local dielectric constant around the Al atoms in the HfAlO$_x$(N) films was measured by XPS at the Institute of Space and Astronautical Science, Kanagawa, Japan. The Al 2p photoelectron spectrum and Al KLL Auger spectrum were measured using an Al Kα X-ray source [2]. The modified Auger parameter $\alpha'$ is obtained by summing up the binding energy of the Al 2p peak and the kinetic energy of the Al KLL peak. The shift in the Auger parameter $\Delta \alpha'$ was determined with respect to that of metal Al (1466.10 eV).

It is known that there is a linear correlation between $\Delta \alpha'$ and $(1-1/\varepsilon)$, which is a function of the optical dielectric constant $\varepsilon$ [3]. Figure 2 shows the correlation between $\Delta \alpha'$ and $(1-1/\varepsilon)$ for Al compounds, which is obtained by plotting the data of ref. 3. The local dielectric constant for the HfAlO$_x$(N) films was estimated from the measured $\Delta \alpha'$ values by using the straight line in Fig. 2.

Figure 1. Schematic view of optics of extremely asymmetry.

Figure 2. Correlation between the shift in the Auger parameter $\Delta \alpha'$ and $(1-1/\varepsilon)$. 

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y = -0.0801x + 1
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3. Results and discussion

3.1. Strain field

Figure 3 shows the integrated logarithmic intensities of the calculated rocking curves of the Si 113 reflection of the Si (001) substrate. Each point in Fig. 3 corresponds to one rocking curve the Si 113 reflection. This calculation is based on Darwin’s dynamical diffraction theory [5–7]. In a distorted crystal model, it was assumed that the strain is largest at the topmost surface and attenuates in direction of the depth of the crystal like a Gaussian function. This model is characterized by the parameters $\Delta d$ and $H$. $\Delta d$ is the strain of the topmost (001) spacing with respect to the bulk value and is defined as $\Delta d = (d-d_0)/d_0$ where $d$ is the (001) spacing of the topmost layer and $d_0$ is the (001) spacing of the bulk. $H$ is the thickness of the distorted layer. In this calculation, it is assumed that $H$ is 40 nm. The integrated intensities of versus wavelength curve is represented approximately by a straight line as shown in Fig. 3. If compressive strain is present, the slope of the line is decreased, while tensile strain increases the slope.

Figure 3. The integrated logarithmic intensities of the calculated rocking curves of the Si 113 reflection of the Si (001) substrate vs the X-ray wavelength.

Figure 4 shows the integrated logarithmic intensities of the measured rocking curves. Figure 5 shows the slope calculated from Fig. 4. For the samples with PDA, the slope is almost the same for different in-situ annealing temperatures. On the other hand, for the sample without PDA, the higher the in-situ annealing temperature is, the smaller the slope becomes. So we conclude that compressive strain is introduced in the case of the sample without PDA and that the strain is reduced by PDA.

Figure 4. Dependence of the integrated logarithmic intensities on the X-ray wavelength for different in-situ annealing temperatures in an NH₃ ambient. (a) samples without PDA, (b) samples with PDA. Circles, triangles, rhombuses denote in-situ annealing temperatures of 750°C, 850°C, and 950°C, respectively.
We could not specify the exact value of $\Delta d$ and $H$ from analysing the absolute value of slope in Fig. 5, because absolute value of integrated logarithmic intensity in Fig. 3 and 4 largely depends on the interval of integration. However, the tendency of compressive strain decreases the slope and tensile strain increases the slope is independent of the interval.

The compressive strain for all the samples was also confirmed by the rocking curve fitting. The typical result of curve fitting is shown in Fig. 6. Detailed analysis will be published elsewhere.

It was reported that a lower temperature annealing introduces less nitrogen, while a higher temperature results in more nitrogen [8]. In the case of the sample without PDA, there is a possibility that the amount of the nitrogen in the interlayer SiO$_2$ film is larger for higher in-situ annealing temperatures. The nitrogen rich interlayer SiO$_2$ film may give the strong compressive strain. On the other hand, for the sample with PDA, it is thought that the PDA process structurally relaxes the compressive strain.

3.2. Results by XPS

Table I shows the Auger parameter $\alpha'$ and $\Delta \alpha'$ of each sample. We calculated the dielectric constant near the Al atoms by using Table I and Fig. 2. The result is shown in Fig. 7. For the samples without PDA, the higher the substrate temperature is, the lower the local dielectric constant becomes. For the samples with PDA, only small differences are observed.

| In-situ annealing temperature [°C] | Modified Auger parameter [eV] | $\alpha'$ | $\Delta \alpha'$ |
|-----------------------------------|-------------------------------|---------|---------------|
| without PDA                       |                               |         |               |
| 750                               | 1462.06                       | 4.04    |               |
| 850                               | 1461.93                       | 4.17    |               |
| 950                               | 1461.66                       | 4.44    |               |
| with PDA                          |                               |         |               |
| 750                               | 1461.88                       | 4.22    |               |
| 850                               | 1461.85                       | 4.25    |               |
| 950                               | 1461.96                       | 4.14    |               |

Table I. Modified Auger parameter of each sample.
We found that there is a correlation between the lattice strain and the local dielectric constant near the Al atoms from Fig. 5 and Fig. 7.

4. Summary
We studied the strain fields near the HfAlO$_x$(N)/SiO$_2$/Si interface by the extremely asymmetric X-ray diffraction and the local dielectric constant near the Al atoms by XPS. For the samples with PDA, there is no difference in the lattice strain and the local dielectric constant between samples with different in-situ annealing temperatures. In the samples without PDA, more compressive strain and a smaller local dielectric constant were observed for higher in-situ annealing temperatures. The experiments show a correlation between the lattice strain and the local dielectric constant near Al atoms.

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References
[1] T. Emoto, K. Akimoto, Y. Yoshida, T. Nabatame, and A. Toriumi: Appl. Surf. Sci. 244 (2005) 55.
[2] K. Hirose, H. Kitahara, and T. Hattori: Phys. Rev. B67 (2003) 195313.
[3] F. Filippone and G. Moretti: Appl. Surf. Sci. 135 (1998) 150.
[4] A. Toriumi, K. Iwamoto, H. Ota, M. Kadoshima, W. Mizubayashi, T. Nabatame, A. Ogawa, K. Tominaga, and H. Satake: Microelectronic Engineering 80 (2005) 190.
[5] T. Emoto, K. Akimoto, A. Ichimiya, and K. Hirose: Appl. Surf. Sci. 190 (2002) 113.
[6] T. Takahashi and S. Nakatani: Surf. Sci. 326 (1995) 347.
[7] W. Yashiro, Y. Ito, M. Takahasi and T. Takahashi: Surf. Sci. 490 (2001) 394.
[8] T. Nabatame, K. Iwamoto, K. Yamamoto, K. Tominaga, H. Hisamatsu, M. Ohno, K. Akiyama, M. Ikeda, T. Nishimura, H. Ota, T. Horikawa and A. Toriumi: J. Vac. Sci. Technol. B22, (2004) 2128.