Depth Profiling of Silicon Nitride Films Prepared by Plasma Anodization

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X-ray photoelectron spectroscopy has been used to study the chemical structures of silicon nitride films prepared by plasma anodization. The Si_3N_4/Si interface was studied by chemical depth profiling. It is found that SiO_xN_y exist within 3 nm of the interface and at the surface, but with nearly ideal silicon nitride in the rest of the film. Nearly same distribution of SiO_xN_y near the interface is found for all the films with thickness range from 5.6 to 15.6 nm. The possible mechanism of plasma anodic nitridation which can explain these results are discussed.

§1. Introduction

The plasma anodic nitridation of silicon is an attractive technique for ULSI fabrications because thick silicon nitride films can be formed at low temperature by using this technique. According to Auger depth profiling, amounts of oxygen near the interface in this case are less than those for silicon nitride films deposited by LPCVD[1,2]. In order to investigate the structural origin of this difference, the chemical structures of the films were studied by using X-ray photoelectron spectroscopy.

§2. Experimental Details

The plasma anodic nitridation of <100> oriented silicon wafers with p-type resistivity of 20 Ωcm was performed at 900 °C in the mixture of hydrogen and nitrogen at 1 torr with 13.56 MHz rf power of 200 W and 112 V dc bias voltage. The starting thickness of silicon nitride films studied are in the range from 5.6 to 15.6 nm. Depth profiling was performed

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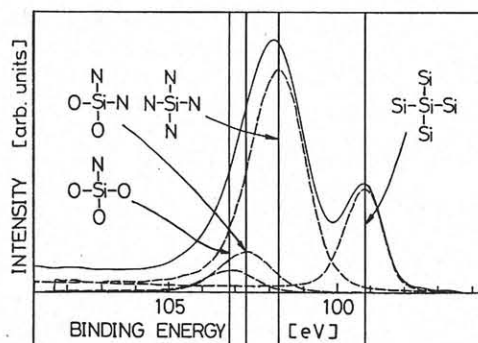**Present address: Tokyo Laboratory, Koa Denko Co. Ltd., 3-2-3 Ebisu, Shibuya-ku, Tokyo 150, Japan

by using a dilute HF etching solution ($HF:CH_3OH:H_2O=1:18:1$), while maintaining solution temperature at 25 °C and with supersonic vibration of the solution. The Si 2p, O 1s, N 1s photoelectron spectra excited by Mg Kα radiation were measured on these nitride films by using microcomputer controlled DuPont ESCA 650B spectrometer. In order to avoid the detection of photoelectrons from the substrate, the corners of the square shaped specimens are covered with a copper mask. The other experimental details are the same as those described elsewhere[3].

§3. Experimental Results

Fig. 1 shows the comparison of Si 2p photoelectron spectra for three specimens; as grown silicon thermal oxide film having thickness of 3.9 nm, as grown silicon nitride film having thickness of 3.7 nm prepared by plasma anodization, chemically etched silicon nitride film having thickness of 4.2 nm prepared by LPCVD. The values of FWHM and chemical shift for these spectra are listed in Table 1. According to this table, the chemical shift observed for plasma anodized film is in between that for LPCVD film and that for thermal oxide film. If we assume that

Table 1

	C.S.(eV)	FWHM(eV)
oxide film	4.52	1.82
PA film	3.43	2.20
LPCVD film	2.82	2.20

PA:Plasma Anodized, C.S.:Chemical Shift

LPCVD film is quite close to ideal Si_3N_4 film, oxynitride(SiO_xN_y) must be included in plasma anodic nitridation film. Here, oxide film was thermally grown in dry oxygen at 800 °C, plasma anodic film was prepared at 920 °C in the mixture of nitrogen and hydrogen at 1 torr with rf power of 300 W and 150 V dc bias voltage. Fig. 2 shows one example of the change in Si 2p photoelectron spectra in depth direction for plasma anodic film having starting film thickness of 9.9 nm. The nitridation induced chemical shift is observed to decrease with decreasing thickness and to increase again in the region close to the interface, exhibiting the existence of oxynitrides on the surface and at the interface. The thickness shown in this figure except 9.9 nm was calculated from the Si 2p spectral intensity for silicon substrate and that for silicon nitride film. Here, electron escape depth is assumed to be constant throughout the film, and to be equal to 2.1 nm obtained for silicon nitride film prepared by LPCVD.
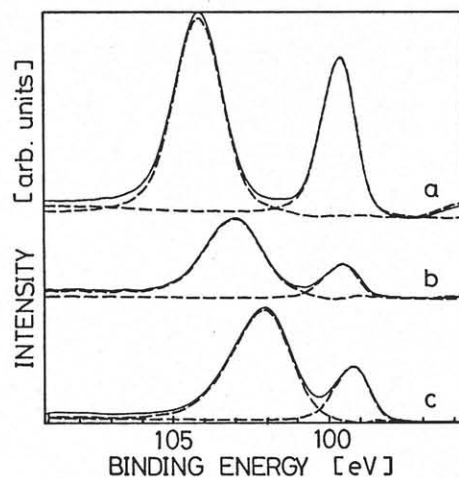
§4. Analysis of Photoelectron Spectra

Fig. 1 Si 2p photoelectron spectra for three specimens; a:oxide film, b:plasma anodic nitridation film, c:LPCVD film.
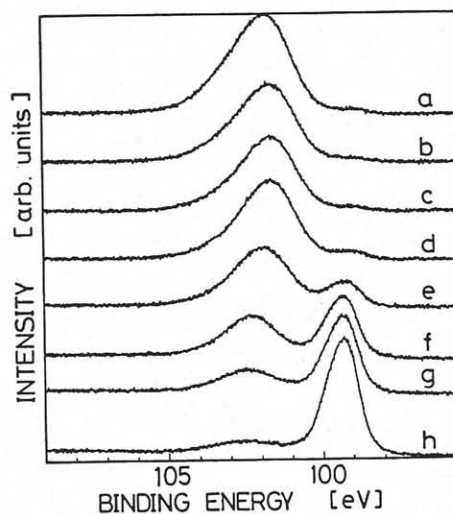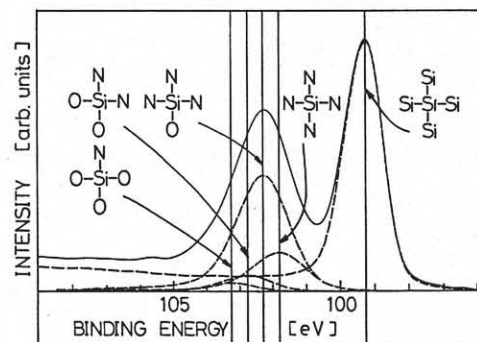

Fig. 2 Depth Profiling of plasma anodic nitridation film with starting film thickness of 9.9 nm; a:9.9, b:8.6, c:8.4, d:7.3, e:4.7, f:2.5, g:1.6, h:0.79 nm, respectively.

(a)

(b)

Fig. 3 (a) and (b) shows deconvolution of spectrum e and f in Fig. 2, respectively.

The Si 2p photoelectron spectra are analyzed with following four assumptions; (1) in the case that the amount of silicon dangling bonds can be neglected in silicon nitride films, 15 kinds of tetrahedral bonding units including Si-N and Si-O bonds exist. Among these 10 configurations includes Si-Si bonds. In the case of silicon thermal oxides, the amount of silicon with Si-Si bonds is at the most equal to 10% of silicon in SiO_2 network[3]. If the amount of Si-Si bonds in silicon nitride film is comparable to that in thermal oxides, the existence of Si-Si bonds in silicon nitride films can be neglected in the first order approximation. Then, the composition of silicon nitride films can be considered to consist of following five components, that is, $SiO_{x/2}N_{(4-x)/3}$, x=0, 1, 2, 3, 4; (2) The amount of chemical shift for each component is assumed to be independent on the thickness of the film so that it increase linearly with increasing x. Here, the chemical shift for Si in Si_3N_4 and that for Si in SiO_2 is assumed to be 2.55 and 4.44 eV, respectively; (3) According to Table 1, FWHM for Si in SiO_2 is smaller than that for Si in Si_3N_4. Therefore, FWHM for each component are assumed to decrease linearly with increa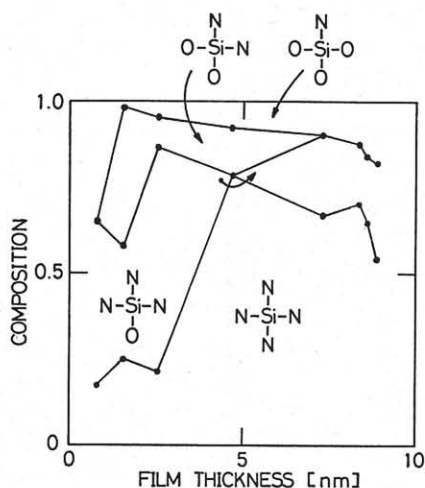sing x. Here, FWHM for Si in Si_3N_4 and that for Si in SiO_2 is assumed to be 1.91 and 1.74 eV, respectively; (4) The lineshape of each component is determined such that the value of FWHM for spectrum obtained from the convolution integral of Si 2p photoelectron spectrum for Si in SiO_2 and Gaussian function satisfies assumption(3). Fig. 3 shows two examples of deconvolution thus obtained.

§5. Discussions

The accurate analysis of Si 2p photoelectron spectra is limited for the thickness range of less than 7 nm, because of small chemical shift for Si in Si_3N_4. Fig. 4 shows the change of the composition in depth direction obtained from the spectral analysis of Fig. 2. The composition shown here is certain average of composition over the range of electron escape depth. From this figure the atomic density ratio R(d) of nitrogen with respect to silicon is calculated as a function of film thickness d as shown in Fig. 5. If the value of electron escape depth in the film and density of silicon atom do not change throughout the film and is equal to Λ and n_s, respectively, R(d) is shown to satisfy the following equation. Here, $n_N f(x)$ expresses the density of nitrogen atom at distance x from the interface, and
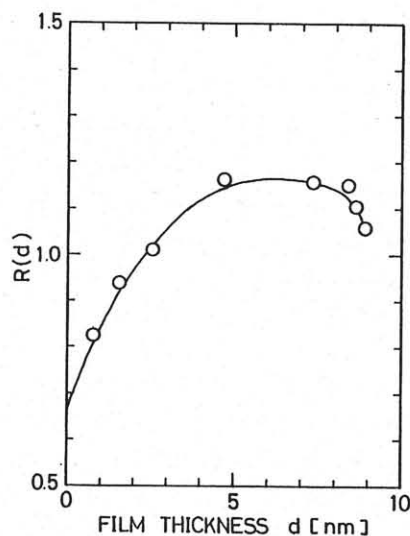

Fig. 4 Compositional change in depth direction for plasma anodic film with starting film thickness of 9.9 nm.

Fig. 5 Atomic density ratio R(d) of nitrogen with respect to silicon as a function of film thickness d.

n_N expresses density of nitrogen atom in Si_3N_4 film.

$$R(d) = \{(n_N/n_s\Lambda)/[1-\exp(-d/\Lambda)]\} \cdot$$
$$\int_0^d f(x)\exp[-(d-x)/\Lambda]dx$$

The distribution function f(d) of nitrogen stom in the plasma anodic nitridation film show2 in Fig. 6 is determined such that R(d) in Fig. 5 satisfies the equation mentioned above. According to Fig. 6, oxynitrides exist within 3 nm of the interface and at the surface, while nearly ideal silicon nitrides are formed in the rest of the films. Almost the same amount of oxynitride near the interface for all the nitride films studied implies that plasma anodic nitridation is mainly due to the transport of nitrogen ion through the oxynitride layer. The present result on the distribution of nitrogen is different from the observation of nitrogen pile up found in thermally nitrided SiO_2 film at 2.5 nm from the SiO_xN_y/Si interface[4,5].

§6. Summary

The chemical structures of silicon

nitride films prepared by plasma anodization has been studied. It is found that oxynitrides exist within 3 nm of the interface and at the surface, but with nearly ideal silicon nitride in the rest of the film. Nearly the same distribution of oxynitride near the interface is found for all the films studied, implying that the plasma anodic nitridation is mainly due to the transport of nitrogen ion through the oxynitride layer.

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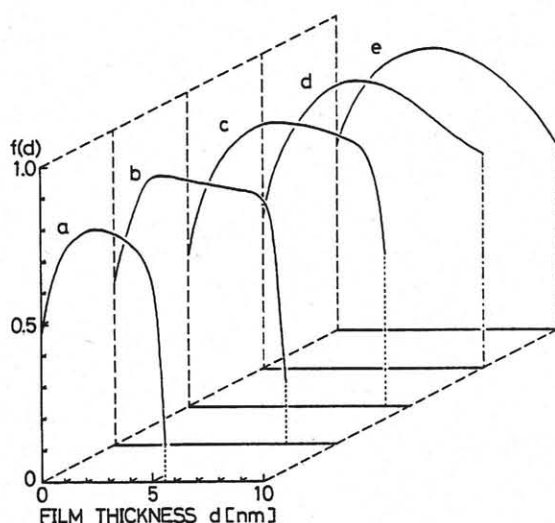5) R. P. Vasquez, A. Madhukar, F. J. Grunthaner and M. L. Naiman: Appl. Phys. Lett. 46(1985)361.

Fig. 6 The distribution function f(d) of nitrogen atom in the plasma anodic nitridation film as a function of d with starting film thickness as a parameter; a:5.6, b:7.7, C:9.9, d:12.4, e:15.6 nm, respectively. These five thicknesses were determined by ellipsometric measurements.