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Structural and chemical characterization of 4.0 nm thick oxynitride films

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We report x-ray reflectivity and secondary ion mass spectrometry (SIMS) analysis of several silicon oxynitride films of 4.0 nm thick as a function of nitrogen concentration at the interface between the oxide and the Si substrate. The x-ray reflectivity data have been analyzed using a model-dependent matrix method, and the results were compared with the model-independent method based on the distorted wave Born approximation and Fourier inversion refinement technique based on the Born approximation. Limitation of each of these techniques is also discussed. The x-ray reflectivity analysis of the films reveals the existence of high electron density at the region where nitrogen accumulation has been observed. Nitrogen accumulation has been observed using dual-beam time-of-flight-SIMS. The results of x-ray reflectivity have been compared with the results of SIMS.
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Dielectric films of oxynitride have replaced pure silicon oxide films as gate and tunnel oxide films in the ultralarge scale integrated technology because of superior properties in terms of the boron barrier, resistance to electrical stress, and higher dielectric strength. The exact mechanism of the role of nitrogen in inhibiting boron diffusion is not completely clarified, although evidence of chemical interaction between boron and nitrogen has been reported.[1] The most interesting aspect is that the nitrogen places itself at the interface of SiO_2/Si independent of how it has been introduced either by (NO or N_2O), and also independent of the condition of preparation.[2,3] Characterization of nitrogen distribution in oxynitride thin films is becoming a very challenging task, given the extreme low thicknesess used in today's technology. The structural and chemical characterization of the oxynitride film in the present study have been done using grazing incidence x-ray reflectivity (GIXR) and dual beam time-of-flight-secondary ion mass spectrometry (TOF-SIMS). From the analysis of the x-ray reflectivity measurement on thin films, one can infer the electron density profile (EDP) across the film depth,[4] roughness at the interfaces and also to a certain extent the chemical composition by proper modeling of the structure of the film.[4,5] In this article, we show the correlation between the chemical composition of the oxynitride and its structural implication by comparing TOF-SIMS depth profiling with GIXR.

In the present investigation, we used five different oxynitride film, grown from 3.5 nm wet oxides, by nitridation in a NO/N_2 atmosphere with an increasing NO concentration from 0% to 100% (samples A to E). Longitudinal specular and off-specular data were collected for GIXR measurement using a laboratory x-ray source of wavelength 1.54 Å, the off-specular intensity from all samples were found to be very small having the value close to background counts. Dual beam TOF-SIMS was used for N depth profiling.

In Fig. 1, we show specular x-ray reflectivity for samples A to E. We clearly observe a gradual evolution of the reflectivity profile in terms of amplitude of oscillation as a function of the increase in N concentration. To calculate the reflectivity as a function of scattering wave vector Q_Z, one requires the exact layer thicknesses involved in the film (t), the electron density (ρ) of each of those layers and of the electron density gradient "$d\rho/dz$" involved at each of the interfaces. The gradient in the electron density at the interface can arise from height–height fluctuations if the interface is seperated by two different chemical species which is generally known as "roughness" or due to chemical diffusion across the interface or mass density gradient along the depth of the film. The later two types are known as graded interfaces. If the electron density gradient "$d\rho/dz$" has a Gaussian form, then the reflectance coefficient at each of the interface is multiplied by a Debye–Waller factor-like term, i.e., by a factor of $\exp(-Q_l^2\sigma_l^2/2)$ where σ_l is the full width at half maximum (FWHM) of the Gaussian distribution of the derivative of electron density ($d\rho/dz$) of the lth layer. These parameters mentioned ($t,\rho,d\rho/dz$), can be adjusted by nonlinear least-square procedures so as to calculate the x-ray reflectivity using Parrat's recursive formula or the matrix technique.[6,7] It is important to note that the Debye–Waller term contains the information about the interface roughness, interdiffusion, and mass gradient at the interface. Precise analysis of the x-ray reflectivity data together with the diffuse off specular allows one to discriminate between interfacial roughness corresponding to height–height fluctuation and electron density gradient corresponding to the graded interface.

Parrat's formalism and the matrix method are the model-dependent method i.e., one has to specify in the beginning of the fitting procedure how many layers one has to consider to

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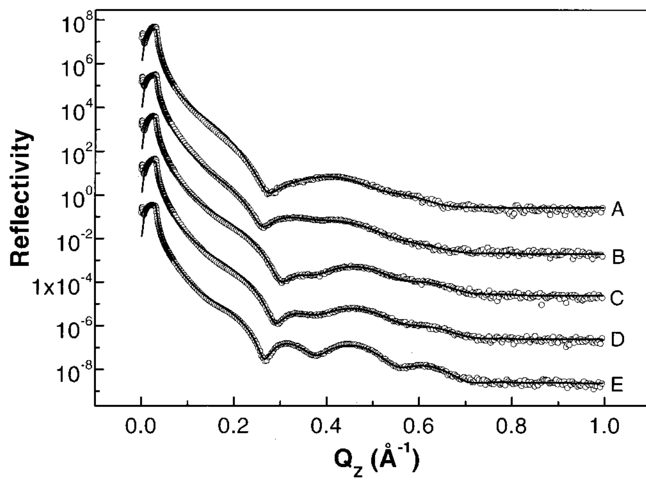

FIG. 1. Specular x-ray reflectivity of samples A to E, solid lines are the fit obtained from the matrix method.

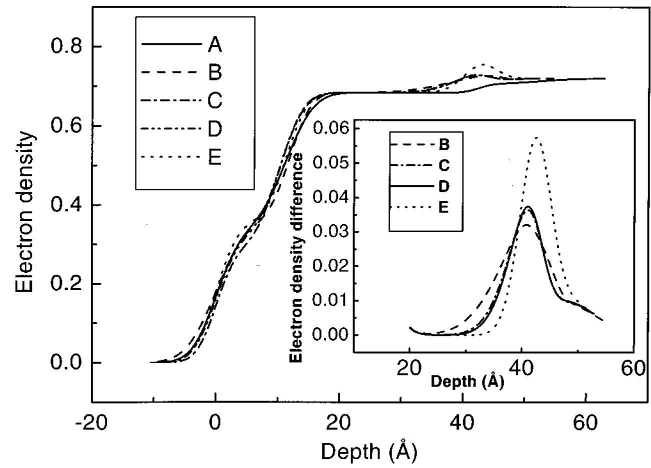

FIG. 2. Electron density profile of samples A to E. Inset: Difference of electron density with respect to sample A.

obtain the best fit of the measured data. We will also consider the model-independent method based on the distorted wave Born approximation (DWBA)[5] and Fourier inversion technique based on the Born approximation (BA)[8–10] to compare the results of each of the methods. First, we have used the matrix method to calculate the EDP. We assumed that the total film on the substrate consisted of mainly three layers. The clue for considering three layers was obtained from the SIMS data which shows an accumulation of N at the interface of the SiO_2 (film) Si (substrate). The N-enriched part of the film was considered as one layer. In addition, we found that the first minimum in the x-ray reflectivity data comes from the top layer. Its thickness was adjusted so as to match the location of the calculated minimum with the one observed in the measured reflectivity data. The third layer in the middle consisted of the rest of the film, i.e., SiO_2. The best fits obtained are shown as solid lines in Fig. 1 and the corresponding parameters obtained are shown in Table I. Figure 2 shows the obtained electron density profiles for different N concentration. In the inset of Fig. 2 we have shown the electron density difference with respect to sample A (zero percent partial pressure of NO). We also observe an increase of the peak height of the electron density as a function of increasing partial pressure of NO. In Fig. 3, we show quantitative nitrogen depth profiles of the samples B to E (sample A has very low nitrogen content) obtained with TOF-SIMS. Peak concentration of nitrogen is placed at the interface Si/SiO_2 and the peak width (FWHM) is around 2 nm, which is the limit of depth resolution of the technique. The EDP in the inset of Fig. 2 presents some similarities with the SIMS profiles, nevertheless, it does not scale proportionally to nitrogen concentration. This arises due to the limitation of the model-dependent method, since the electron density was made to evolve with the restriction of only three boxes of different sizes. One can use this matrix method by considering many boxes but then there will be too many floating parameters to fit and in nonlinear least square fitting one can get unphysical EDP giving rise to false interpretation of the result. To sort out the discrepancy of the area under the EDP profile as a function of an increase in N concentration, we performed a x-ray reflectivity calculation using a model-independent approach as carried out earlier in the framework of DWBA and also a Fourier inverse technique based on BA on the sample having the highest N concentration i.e., sample E. The details of this analysis scheme has been published earlier in detail.[4,5,8–10] Based on the aforementioned two techniques, the reflectivity curves obtained are shown in Fig. 4. The EDP obtained from these two formalisms are shown in the inset of Fig. 4. Both formalisms give the same result i.e., the EDP falls on each other. In the same inset of

TABLE I. Value of critical wave vector Q_c (Å^{-1}), σ (Å) and thickness t (Å) [$Q_c/\sigma/t$].

	Substrate	N-rich region	SiO_2 layer	Top layer
Sample A	0.0318/4.6/**	0.0315/1.9/10.0	0.0310/3.6/31.2	0.0217/3.1/11.2
Sample B	0.0318/1.7/**	0.0322/5.8/7.6	0.0310/2.7/26.2	0.0225/3.8/11.9
Sample C	0.0318/2.0/**	0.0326/4.4/4.1	0.0310/3.2/29.6	0.0201/2.5/10.1
Sample D	0.0318/2.0/**	0.0327/4.1/3.7	0.0310/3.0/29.5	0.0213/2.9/10.4
Sample E	0.0318/2.3/**	0.0343/3.0/2.7	0.0310/2.7/30.3	0.0224/2.8/11.3

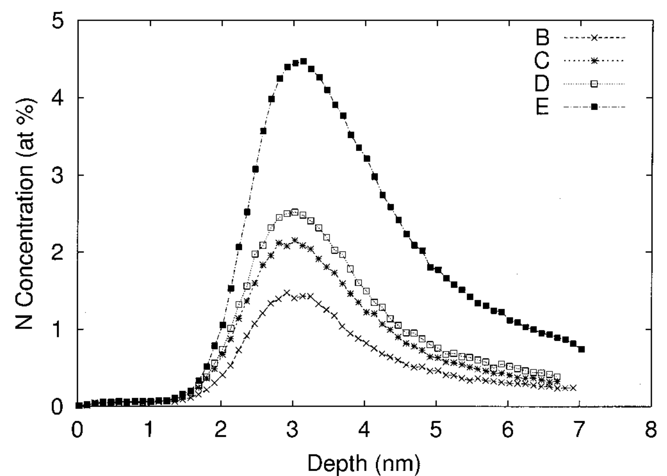

FIG. 3. Nitrogen depth distribution obtained with TOF-SIMS for sample A to E.

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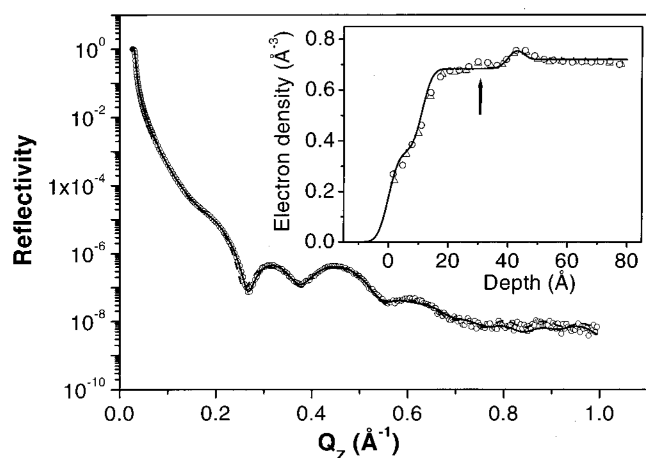

FIG. 4. Specular x-ray reflectivity curves obtained from model-independent using DWBA formalism (solid line) and from Fourier inversion technique using BA (dashed line). Inset: Electron density profile obtained with the model independent technique (triangles), Fourier inverse technique (circles) and the matrix method (solid line).

Fig. 4, we have plotted the EDP obtained by the matrix method for sample E. At first look, it appears that all the results agrees quite well with each other, but at a closer look, we see a small hump in the middle region layer marked by an arrow in Fig. 4. For samples with a lower N concentration, this hump was not observed and the variation in the EDP was very difficult to observe to say anything with certainty. The smaller area under the curve and low value of FWHM in the EDP of sample E (see Fig. 2) may be due to the fact that the variation of electron density in the middle layer was not considered in the matrix method.

The electron density of the top layer convoluted with σ in the matrix method describes very accurately the gradient of electron density as obtained by the other two techniques. Since the variation of the electron density obtained from the matrix method continues from the surface of the film up to $\sim$10 Å depth, this clearly indicates that the electron density convoluted with σ is not the surface roughness due to height–height fluctuation, but it is the electron density gradient as obtained by the other two techniques. Convolution of electron density ρ with σ and thickness t gives the EDP which is the profile of the scattering potential of the total film. Thus, the contribution of σ for the present system studied is mainly due to interdiffusion and mass density gradient and in such a case, the value of thickness t and σ can be comparable as can be seen in the Table I. The more meaningful quantity is the final profile of the scattering potential obtained from the fit i.e., the EDP obtained from the analysis of the specular x-ray reflectivity data. Thus, one has to be careful in interpreting the σ obtained from fitting the Parrat's formula or matrix method: The cause of the increase of electron density at the interface of SiO_2/Si is still not understood though there is some speculation of the formation of silicon nitride[11] at the interface giving rise to an increase of electron density.

To summarize, the accumulation of N was observed by SIMS analysis at the interface of SiO_2/Si. X-ray reflectivity analysis shows a systematic increase of electron density with the increase of N concentration at the interface of SiO_2/Si. To analyze the x-ray reflectivity data for ultrathin samples such as in the present work, one has to be careful with the interpretation of the result obtained using Parrat's formula or the matrix method. The result depends on the number of boxes being considered to describe the total thickness of the film. The parameter σ obtained from the matrix method is the FWHM of $d\rho/dz$ arising from interdiffusion or mass density gradient rather than just the interfacial roughness due to height–height fluctuation at the interface.

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