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Characterization of silicon/oxide/nitride layers by x-ray photoelectron spectroscopy

Walter Hansch, Anri Nakajima, and Shin Yokoyama
Research Center of Nanodevices and Systems, Hiroshima University, 1-4-2 Kagamiyama, Higashi-Hiroshima 739, Japan

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Core-level intensities for Si 2*p*, Si 2*s*, O 1*s*, and N 1*s* were measured by x-ray photoelectron spectroscopy in bulk samples of silicon, SiO_2 and Si_3N_4. A complete and consistent set of intensity ratios is given and applied for calculations of thickness and stoichiometry in thin Si/oxide/nitride layers, which can be used for gate dielectrics in advanced metal–oxide–semiconductor field-effect transistor fabrication. © *1999 American Institute of Physics.* [S0003-6951(99)03037-5]

Silicon oxynitrides are promising candidates for advanced metal–oxide–semiconductor field-effect transistor (MOSFET) gate dielectrics. In *p*-MOSFETs with gate oxide thickness of only a few nanometers, the through diffusion of boron from p^+-poly gate can be suppressed by incorporating nitrogen in the oxide layer via various techniques.[1,2] But recently it was found that the diffusion of nitrogen also takes place and degrades transconductance dramatically.[3] For this reason, we adopted a process of self-limited atomic layer deposition (ALD)[4] to deposit stoichiometric nitride on top of the gate oxide and thus prevent the diffusion of both nitrogen and boron atoms. X-ray photoelectron spectroscopy (XPS) is a unique analytical technique for atomically thin layers, but so far few comparable XPS data are available to investigate this important silicon/oxide/nitride system. In this work, we have measured the core level intensities of silicon, oxygen, and nitrogen in bulk samples of Si, SiO_2, and Si_3N_4. Such bulk intensity ratios are essential for any investigation of stoichiometry and layer thickness in this three-component system.

In order to measure the above-mentioned core-level bulk intensities, samples of hydrogen-terminated clean Si (substrate), thermal grown SiO_2 (100 nm) and low-pressure chemical vapor deposition (LPCVD) Si_3N_4 (100 nm) were fabricated using standard MOS technology. The MOSFET samples with nitride/oxide gate dielectrics were fabricated on cleaned Si substrates [(100), *n* type, 10 Ω cm]. Gate oxides were grown at 850 °C for several minutes, resulting in a thickness of a few nanometers that was checked by ellipsometry, XPS, and $C-V$ measurements. Immediately after gate oxidation, the wafers were transferred in an LPCVD furnace for ALD of nitride. One ALD cycle consists of an exposure of SiH_2Cl_2 at 37.5° and a subsequent exposure of NH_3 at 550 °C, resulting in the self-limited deposition of 0.5 atomic monolayer nitride on Si.[5] Depending on the process parameters, the deposition selectivity on SiO_2 can be adjusted.

Samples were investigated by XPS after each of the steps mentioned above. The high-resolution XPS measurements were performed with an ESCA-300, using monochromatic Al K_α radiation (1486.6 eV). The instrumental energy resolution was 0.26 eV, and the small analyzer acceptance angle of 3.3° allowed angle-resolved measurements for the emitted photoelectrons. Wide-range spectra and the Si 2*p*, Si 2*s*, O 1*s*, N 1*s*, and C 1*s* core-level peaks were measured at various photoelectron take-off angles ranging from 5° to 90° for all samples. Bulk samples of Si, SiO_2, and Si_3N_4 spectra were compared by mounting two samples on the same sample holder. In order to keep the measurement conditions for both samples as close as possible, only the sample holder was shifted parallel to the instrumental x-ray and detection geometry for every measurement angle.

The determination of absolute values for binding energies in inhomogeneous, nonconductive materials is difficult to handle due to the lack of a defined Fermi level and to differential charging effects.[6] The Si-substrate Si $2p_{3/2}$ core level was detectable in all ALD samples and was used for energy adjustment at a binding energy of 99.6 eV. This adjustment, which never exceeded 0.3 eV, also shifted the C 1*s* to the 286.0 eV position. With that, it was possible to compare the spectra directly without influencing the determination of intensity ratios.

Figure 1 shows the Si 2*p* core levels of two typical ALD samples. The detection angle of 45° was chosen to show substrate photoelectron peaks as well as overlayer signals of nitride/oxide dielectrics.

The Si 2*p* core level consists of nonoxidized Si^0 from substrate and fully oxidized Si^{4+} in the nitride/oxide overlayers. For substrate silicon Si^0, the Si $2p_{3/2}$ and Si $2p_{1/2}$ dou-

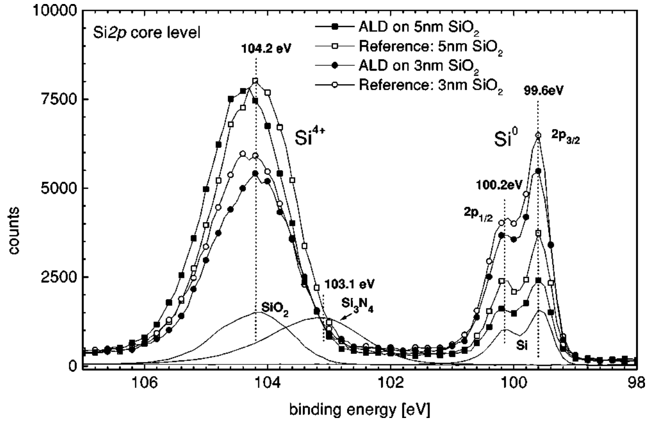

FIG. 1. Typical XPS spectra of Si 2*p* core level for gate oxides with 3 and 5 nm thickness with and without ALD nitride on top. Spectra of bulk Si, bulk SiO_2 and bulk Si_3N_4 are inserted on a low scale for reference. The spectra are adjusted to the Si^0 position of Si $2p_{3/2}$ at 99.6 eV.

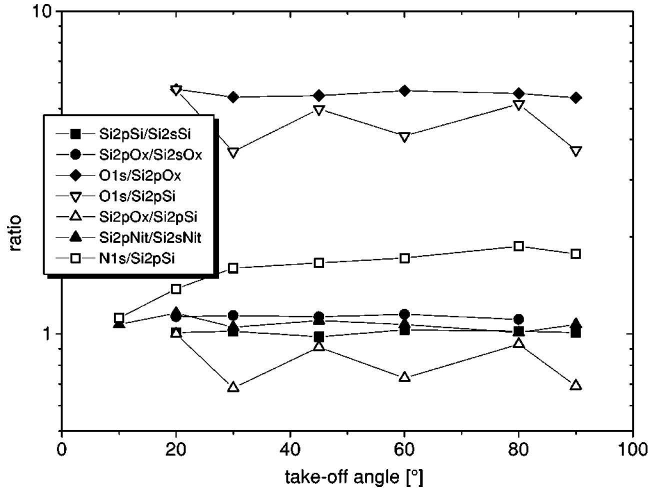

FIG. 2. Angle-dependent intensity ratios for bulk samples of Si, SiO_2, and Si_3N_4. Ratios taken from one material within one spectrum are indicated by filled symbols; these values show a scatter within 5%. Open symbols indicate ratios of different samples. Small variations in the measurement parameters will introduce a uncertainty of about 20% in the ratios. Core levels are noted, for example, Si 2*p*Si or Si 2*s*Ni*t* for a Si 2*p* signal from Si bulk or Si 2*s* from nitride, respectively.

blet from the spin-orbit coupling is resolved and shows the good energy resolution of the measurement. Depending on the bonding partner and its electronegativity, the Si 2*p* core level shifts to higher binding energies. This so-called chemical shift to fully oxidized Si^{4+} can be seen for the samples investigated. The well-known existence of suboxides (Si^{1+}, Si^{2+},...) and subnitrides in atomic monolayer films will result in intermediate peak positions. Other effects will introduce unknown shifts in the core-level energies, e.g., Fermi level pinning due to interface states and relaxing to its bulk value depending on substrate doping by hydrogen annealing[7] or sample-specific or thickness dependent shifts due to differential charging effects of particular core-level energies.[8] Such a sample-specific shift to higher energies can be seen in Fig. 1 for the Si^{4+} in the ALD samples compared to the pure oxide samples. For the determination of stoichiometry, the core-level intensities of N 1*s* or O 1*s* with the corresponding oxidized Si 2*p* core levels must be compared. Taking into account all the above-mentioned, possible peak shifts of the Si 2*p* core level, a reliable determination of nitride stoichiometry on/in gate oxides seems to be a challenging task for an extremely careful data deconvolution. The situation is the same for the intrinsically broader Si 2*s* core level. The Si 2*s* signal was measured to investigate the influence of the so-called Reilman asymmetry factor for angle-dependent emission from different kind of orbits $(s,p,...)$.[9]

This problem with the indistinguishable Si 2*p* levels is circumvented by using the well-separated core levels of either N 1*s* (~398 eV) or O 1*s* (~533 eV) along with either Si^0 2*p* (~100 eV) or Si 2*s* (~150 eV) from bulk. But in this case, it is not the stoichiometry within the overlayer that can be calculated, but only the total amount of non-silicon atoms. If a particular stoichiometry is assumed, a layer thickness can be deduced from this value.

TABLE I. Experimental XPS core-level ratios for bulk samples of Si, SiO_2, and Si_3N_4; along with published values to our knowledge. The values represent the mean value $\langle x \rangle$ for all measured take-off angles and the standard deviation σ.

Ratios out of one material				
Ratio	Si 2*p*Si/ Si 2*s*Si	Si 2*p*O*x* / Si 2*s*O*x*	Si 2*p*Ni*t* / Si 2*s*Ni*t*	
This work	1.00	1.13	1.05	
$\langle x \rangle \pm \sigma$	±0.05	±0.01	±0.05	
Literature				
Ratio	O 1*s*/ Si 2*p*O*x*	O 1*s*/ Si 2*s*O*x*	N 1*s*/ Si 2*p*Ni*t*	N 1*s*/ Si 2*s*Ni*t*
This work	5.5	6.3	1.7	1.8
$\langle x \rangle \pm \sigma$	±0.2	±0.2	±0.1	±0.1
Literature			1.95[a]	
Ratios for different materials, noted as *K* in the following text				
Ratio	Si 2*p*O*x* / Si 2*p*Si	Si 2*s*O*x* / Si 2*s*Si	O 1*s*/ Si 2*p*Si	O 1*s*/ Si 2*s*Si
This work	0.82	0.82	4.6	4.6
$\langle x \rangle \pm \sigma$	±0.15	±0.15	±0.8	±0.8
Literature	0.82[b]			
Ratio	Si 2*p*Ni*t* / Si 2*p*Si	Si 2*s*Ni*t* / Si 2*s*Si	N 1*s*/ Si 2*p*Si	N 1*s*/ Si 2*s*Si
This work	1.3	1.2	2.4	2.1
$\langle x \rangle \pm \sigma$	±0.1	±0.1	±0.2	±0.2
Literature	1.16[c]			

[a] Reference 11.
[b] Reference 12.
[c] Reference 13.

Peak positions and peak intensities were determined by Gaussian fitting after subtraction of background by using the Shirley method.[10] Other methods of background subtraction or curve fitting resulted in differences of about 5% in the peak area calculation. Figure 2 shows a selection of angle-dependent variation of measured ratios for the various core levels from the bulk samples.

For the bulk samples, it can be seen from Fig. 2 and Table I that the ratio of Si 2*p*/Si 2*s* in Si, SiO_2, and Si_3N_4 is close to unity, without significant dependence on take-off angles; so the influence of Reilman factor is below 5%. The ratios for the elemental signals (O,N) compared to Si differ significantly from unity, thus reflecting a higher atomic density and photoionization cross section. These ratios must be calculated from different samples with more or less changing measurement conditions. Therefore, the ratio values are scattering for various take-off angles, with a standard deviation σ of about $\sigma \sim 20\%$ around the mean value for all take-off angles. Other ratios can be calculated from the ratios given in Table I e.g., N 1*s*/Si 2*p*O*x* = (2.9 ± 0.6) or N 1*s*/O 1*s* = (0.5 ± 0.1).

Quantitative evaluations in the Si/oxide/nitride system are possible with the bulk ratios *K*. Assuming homogeneous and smooth layers, the thickness d_c of thin coverlayers can be calculated from the exponential attenuation law of intensity resulting in Eq. (1):

$$d_c = \lambda_c \sin(\alpha) \ln\left[\frac{I_c(\text{meas})}{I_b(\text{meas})} \cdot \frac{1}{K} + 1 \right], \tag{1}$$

where $I_c(\text{meas})/I_b(\text{meas})$ is the measured intensity ratio of chosen core levels for coverlayer and bulk and *K* represents the same ratio, but for bulk samples as given in Table I, λ_c is the escape depth for photoelectrons in the coverlayer and

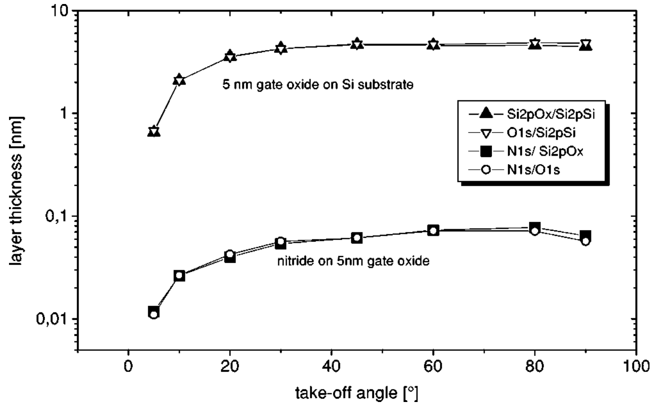

FIG. 3. Calculation of layer thickness for 0.5 monolayer nitride on 5 nm gate oxide. The experimental intensity ratios shown in the legend were taken from Table I. An escape depth of $\lambda_{\mathrm{Ni}t}=3.4$ nm is used.

sin(α) exhibits the dependence on take-off angle. For the calculation of gate oxide thickness, we use the values of $\lambda_{\mathrm{Si}\,2p\mathrm{O}x}=2.9$ nm given recently by Lu *et al.*[14] and the experimentally determined ratio Si 2pOx/Si 2pSi = 0.82 or O 1s/Si2pSi = 4.6. Equation (1) is also used to calculate the thickness of the deposited nitride layer on the top of the gate oxide. In this case, the ratios of N 1s/Si 2pOx and N 1s/O 1s are used, taking the gate oxide as substrate. The escape depth in nitride can be calculated by comparing the densities of atoms in Si and Si_3N_4, which results in a value of $\lambda_{Si_3N_4}\sim 3.4$ nm.

The results of these calculations are shown in Fig. 3 for a 0.5 monolayer nitride deposited in one ALD cycle on a 5 nm gate oxide on a Si substrate. It should be noted that the experimental values result in the same oxide or nitride thickness regardless of whether the Si 2p ratios or O/Si 2p are used. This indicates that the determined ratios are reliable and consistent with one another. The slight slope in nitride thickness with increasing take-off angle is due to the reduced capability of the underlying gate oxide to act as a substrate; the deviation from a constant value for angles below 20° is due to the instrumental function.

In summary, we have presented angle-dependent values of XPS core-level ratios for the Si/nitride/oxide system. No angle-dependent irregularities are observed. The reliability and consistency have been demonstrated by achieving the same results for layer thickness with various ratios. These ratios can be used to carry out quantitative evaluations in oxide/nitride dielectrics for future MOSFET fabrication.

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