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Valence band offset at silicon/silicon nitride and silicon nitride/silicon oxide interfaces

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Abstract

The valence band electronic structure of silicon nitride (Si_3N_4) is studied using the first principal quantum chemical calculation, X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). Assuming that the valence band is formed with N 2p and Si 3s, 3p and 3d electrons and based on the XPS and UPS results, the valance band offset at the Si/Si_3N_4 interface was estimated to be 1.5 ± 0.2 eV. This hole barrier explains the hole dominating conduction in Si/Si_3N_4 structure when a positive potential is applied to the silicon substrate. In addition, the UPS study reveals that the valence band offset at the Si_3N_4/silicon oxide interface is 2.5 ± 0.2 eV.
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1. Introduction

Triple oxide–nitride–oxide (ONO) dielectrics structure is now widely used in various kinds of silicon devices. In electrically erasable read only memory (EEPROM) devices, such dielectric is used to localize electrons and holes for memory effect [1,2]. In dynamic random excess memory, triple dielectric is used in the memory capacitors. In multiple-layer interconnection, ONO structure is used as inter-polysilicon insulator. Since the bottom oxide thickness in the ONO dielectric is usually very thin (in the range of 1.5–2.5 nm), the carrier injection could be very pronounced and the carrier injection is governed by the offset of the valence band in this multiple-layer dielectric.

Although the valence band structures of silicon oxide (SiO_2) and silicon nitride (Si_3N_4) have been studied for approximately three decades, the valence band offset at Si/SiO_2 interface is still uncertain so far. And the valence band offset at the SiO_2/Si_3N_4 interface is still unknown. By separating the carrier injection in Si/SiO_2/Si_3N_4/Al structures [3–5], it was shown that the carrier injection, regardless of the polarity, is dominated by the carrier flowing from silicon to the dielectric near the silicon/dielectric interface. A similar conclusion was also obtained by Bachhofer et al. [2]. However, Weinberg and Pollak proposed a different picture that the current conduction in Si_3N_4 was dominated by hole at both polarities [6]. Further detailed band structure was revealed experimentally by the optical absorption and the photoemission measurements [7,8]. The electron barrier at the Si/Si_3N_4 interface and the bandgap of Si_3N_4 were found to be 2.0 and 5.1 eV, respectively, [7,8]. Considering the aforementioned experimental results, the barrier for electron and hole at the Si/Si_3N_4 interface should be equal and is approximately 2.0 eV [7,9]. This scenario is often used for interpreting

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the charge transport in the EEPROM with Si_3N_4 film as the gate dielectric.

On the other hand, since the hole barrier (3.8–4.7 eV) was found to be larger than the electron barrier (3.15 eV) at the Si/SiO_2 interface [10], the electron current is much larger than the hole current for carrier injection. It was expected that the electron injection should also dominate over the carrier injection in the $Si/SiO_2/Si_3N_4$ structures as it has the same Si/SiO_2 interface for carrier injection. However, this prediction is contradicted with the experimental results and remains unsolved so far. It was determined by an internal hole photoemission that the hole barrier and the electron barrier at the Si/SiO_2 interface are 3.15 and 3.8 eV, respectively [10,11]. According to these data the 'electrical' gap of thermal SiO_2 should be 8.1 eV. Indeed, determined with optical absorption, photoconductivity, and hole accumulation, Powell and Morad [12] found that the optical gap of thermal oxide is 8.0 ± 0.2 eV. However, with the same optical absorption experimental result obtained by Weinberg et al. [13], the optical gap can be 9.3 eV with an alternate model for interpretation. Thus, if the optical gap is 9.3 eV then the hole barrier at Si/SiO_2 interface should be 5.0 eV which is significantly larger than the other reports [8,11]. Different values of barrier are often found in the literature. For instance, 3.8 eV was used for the barrier for hole injection at the silicon/silicon oxide interface [8] and 4.5 eV was used for the hole injection in thin oxide MOS devices [14]. Hence, the valence band offset at the Si/SiO_2 interface is still uncertain so far although it has been investigated for approximately three decades. The objective of the present paper is to investigate the band structure of the Si_3N_4/SiO_2 interface both experimentally and theoretically.

2. Experiment

For photoelectron spectroscopy study, the starting material is ⟨1 0 0⟩ p-type Si with resistivity of 10 Ω cm. The silicon nitride films were prepared by low-pressure chemical vapor deposition method with mixture of SiH_2Cl_2 and NH_3 at 760 °C. The resulting thickness of the nitride film is approximately 5 nm (measured by an ellipsometer). Thermal oxide with thickness of 4.5 nm on the same substrate was also grown by dry thermal oxidation at 800 °C. Valence band X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were measured with a high-resolution (0.25 eV) Kratos AXIS-HS spectrometer with monochromatic Al Kα source (with excitation energy of 1486.6 eV) and He II line (with energy of 40.8 eV). The photoelectrons were detected at a take-off angle of 60° with respect to the surface (normal direction). Details of this measurement were described in another report [15]. Prior to the XPS and UPS measurements, native oxide on the nitride was etched away in 1:30 HF/methanol solution, and then rinsed in methanol. No sputtering cleaning was made on the samples in order to avoid sputter-induced chemical changes in the surface. The charging effect of nitride and oxide films with thickness of 5 nm was checked using cyclohexane. For binding energy reference, the samples were dipped into cyclohexane and followed by nitrogen blow-dry before putting into the XPS system. It was found that the charging effect is less than 0.1 eV. Charging effect in UPS measurements was checked by varying the intensity of the UV light. No shift in the UPS spectral features was observed. Hence the XPS and UPS measurements on the present samples were made without dipping them into cyclohexane.

3. Results and discussion

For correct interpretation of the XPS and UPS spectra, we performed ab initio density functional theory (DFT) calculation using the Amsterdam density functional (ADF) program [16]. All calculations were made on cluster models with crystalline α-Si_3N_4 fragments. Broken Si–N bonds on the cluster boundaries were passivated with H atoms. For simulating the bulk properties of Si_3N_4 we used a $Si_{19}N_{26}H_{36}$ cluster consisting of 81 atoms with three spheres in different coordination (see Fig. 1). The Kohn–Sham molecular orbits were constructed using Slater-type exponential basis functions. The basis set includes double-zeta basis with 3d polarization functions for all Si atoms. It corresponds to the basis set III in ADF terminology [16]. The position of all Si and N atoms was fully optimized at the non-local DFT level using Becke form of exchange [17] and Lee-Yang-Parr theory [18] for functional correlation. Positions of the terminal H atoms were fixed for representing the embedded nature in the solid.

To ensure that the cluster model is valid for simulating the electronic structure of nitride, we simulated the X-ray emission spectra of bulk Si_3N_4. Calculations were performed in frozen orbital approximation. Dipole matrix elements were calculated between the core (Si 1s, 2p and N 1s) orbit and valence orbits. These matrix elements include, in principle, all inter-atomic matrix elements between Slater-type functions centered on different atoms. The calculated spectra were then broadened by convoluting the Lorentz curves with a width of 0.5 eV. We found that the Si 3d polarization functions must be included in the basis set in order to obtain a correct Si *L* X-ray emission spectra. Our calculation also shows that the contributions of Si *K* and N *K* emission spectra to the non-local transitions are negligible. Bold lines in Fig. 2 depict our calculation results. The experimental results of Si *K*, Si *L* and N *K* spectra taken from a previous report [19] are shown in thin lines for comparison. In general, a good agreement between the

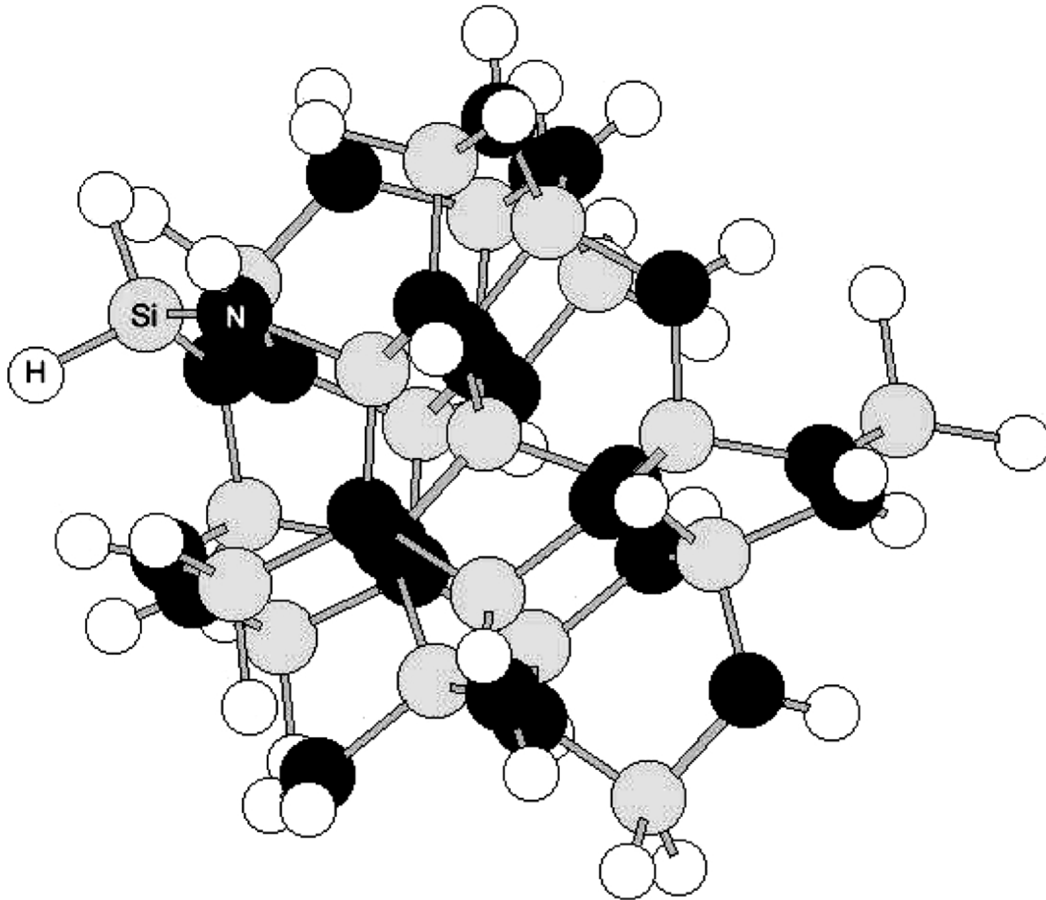

Fig. 1. The 81 atomic cluster $Si_{19}N_{26}H_{36}$ used for simulating the silicon nitride valence band. Hydrogen atoms are not shown in this figure for clarity.

calculated and the experimental data is observed. The simulation results show that the main contributions to the valence band of silicon nitride come from the N 2p, Si 3s, 3p and 3d orbits.

The valence band offset at the Si/Si_3N_4 interface was investigated with an XPS measurement. To calibrate the XPS results, C 1s energy was first measured on gold. Since the work function of gold is 5.0 eV [20], C 1s line energy is found to be 285.2 eV which is determined with reference to the top of valence band of Au. With the C 1s line, the top of the Si valence band (5.0 eV) was then determined with the XPS results. The N 2s peak in Si_3N_4 was calibrated to the vacuum energy and then the N 2s energy was used for determining the top of Si_3N_4 valence band with the UPS results. Fig. 3 shows the XPS spectra of gold, silicon and Si_3N_4 combined to vacuum level. The XPS valence band spectra of silicon nitride and silicon are similar to published results [10,15]. The main contribution in the valence band spectra is related to the excitation of electrons from nitride and silicon and the contribution of carbon on the surface is small. On the other hand, since the escape length for Si 2p electrons in SiO_2 is 2.5 nm [21], the contribution of silicon substrate to nitride XPS spectra is small. The insert in Fig. 3 shows the extrapolated top of the valence band from the XPS spectra. According to Fig. 3, the valence band offset at the Si/Si_3N_4 interface is 1.5 ± 0.2 eV. According to a previous experiment [8] and the present calculations, the top of valence band for silicon nitride is formed by Si s, p electrons and nitrogen 2p electrons. Si 3s electrons dominate near the bottom of the valence band, and around the middle of the valence band Si 3p electrons contribute the major portion. Near the top of the valence band, N 2p electrons dominate. It is noted that the cross-section for the electron ionization in the nitride valence band depends on the wavefunction symmetry and the main contribution to the ionization at 1486.6 eV is due to the Si 3s electrons [22]. Since the Si 3s states dominate the bottom of the valence band, the XPS signal will drop at the top of the valence band and the top position of the Si/Si_3N_4 valence band determined by XPS measurement could be under-estimated. The valence band offset at the Si/Si_3N_4 interface determined in the present work by XPS measurement agrees with the XPS data (1.6 ± 0.2 eV) from Weinberg

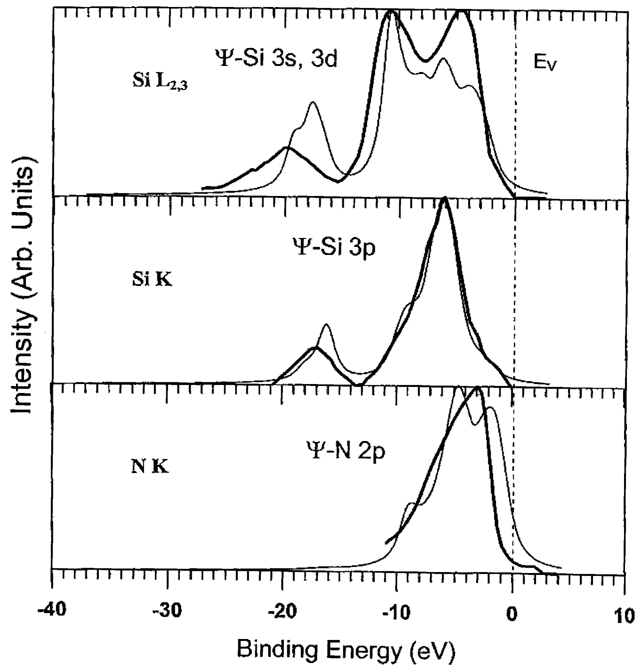

Fig. 2. X-ray emission spectra of silicon nitride calculated using DFT theory (bold lines). Experimental spectra depicted in thin lines [19] are also shown for comparison.

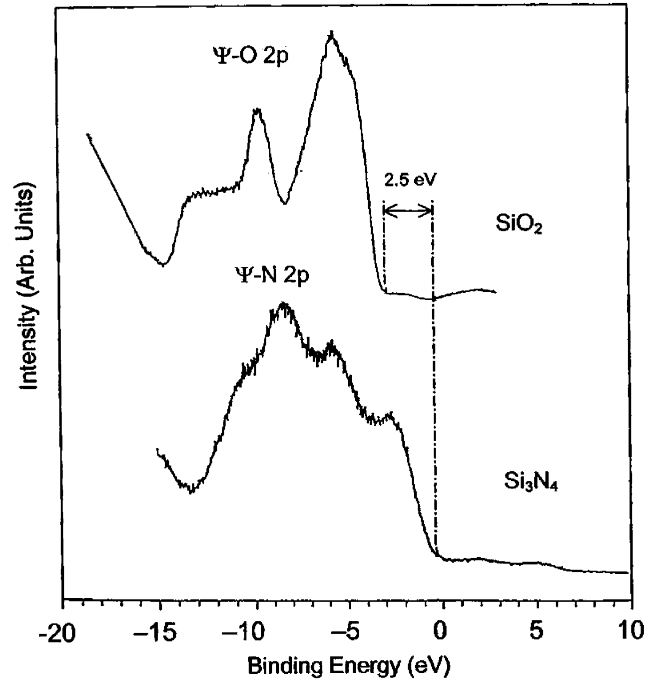

Fig. 4. Ultraviolet photoelectron spectra of thermal oxide and silicon nitride. The excitation energy is 40.8 eV and the estimated valence band offset at the oxide/nitride interface is 2.5±0.2 eV.

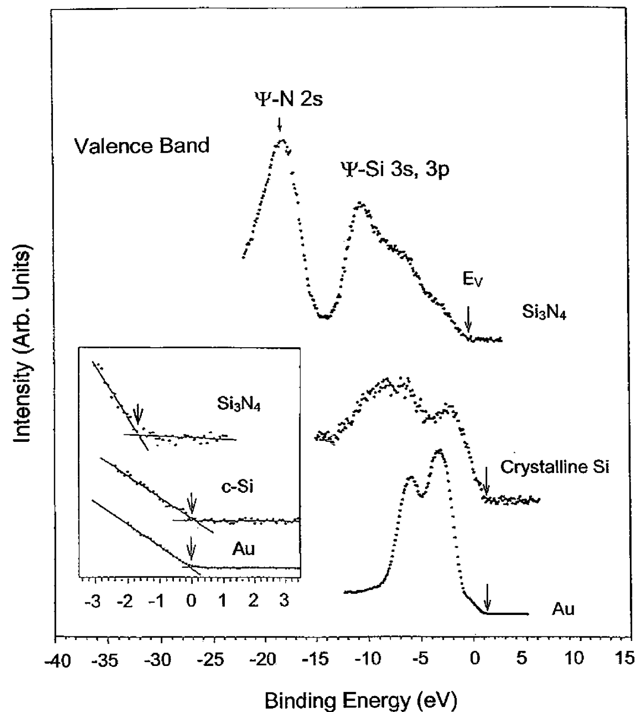

Fig. 3. X-ray photoelectron spectra of silicon nitride, crystalline silicon, and gold. The excitation energy is 1486.6 eV. Insert shows the valence band tail and the extrapolation of this plot gives a valence band offset of 1.5±0.2 eV at the Si/Si_3N_4 interface.

and Pollak [6]. These data are the same as the result obtained from the hole injection study at the Au/Si_3N_4 interface [23]. The value is also close to the valence band offset measured for the amorphous Si/hydrogenized nitride Si_3N_4:H interface [24] which is 1.5±0.1 eV.

To determine the Si_3N_4/SiO_2 valence band offset, we conducted UPS experiment and the results are shown in Fig. 4. With 40.8 eV excitation, it was found that the top of the valence band of Si_3N_4 and SiO_2 are dominated by the N 2p and O 2p electrons, respectively (see the high energy peaks in Fig. 4). In addition, the offset of the Si_3N_4/SiO_2 valence band was found to be 2.5±0.2 eV. According to these data the offset of the Si/SiO_2 valence band should be 4.0±0.4 eV. This value agrees with the experiment of hole photoemission at the Si/SiO_2 interface [11].

4. Conclusions

Using the first principle electronic structure simulation, XPS, and UPS, the valence band electronic structure of silicon nitride is studied. We found that the valence band offset at the Si/Si_3N_4 interface is 1.5±0.2 eV and the valence band offset at the Si_3N_4/SiO_2 interface is 2.5±0.2 eV. We further estimated that the valence band offset at the Si/SiO_2 interface is 4.0±0.4 eV.

Acknowledgments

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