MICROSCOPIC STRUCTURE OF THE SiO₂/Si INTERFACE

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The bonding of Si atoms at the SiO₂/Si interface is determined via high-resolution core level spectroscopy with synchrotron radiation. For oxides grown in pure O₂, the SiO₂/Si interface is found to contain Si atoms in intermediate oxidation states with a density of 1.5 ± 0.5 x 10¹⁵ cm⁻². From the density and distribution of intermediate oxidation states, models of the interface structure are obtained. The interface is not abrupt, as evidenced by the non-ideal distribution of intermediate oxidation states and their high density (about 2 monolayers of Si). The finite width of the interface is explained by the bond density mismatch between SiO₂ and Si. Annealing in H₂ is found to influence the electrical parameters by removing the Pᵦ centers that pin the Fermi level. The distribution of intermediate oxidation states is not affected.

INTRODUCTION

The structure of the SiO₂/Si interface has been elusive despite many efforts to come up with models. Two distinct interface regions have been identified. The near interface is 5Å wide (or less) and consists of Si atoms in oxidation states intermediate between Si and SiO₂. A second region extends about 30Å into the SiO₂ overlayer. The SiO₂ in this region is compressed because the bond density at the Si surface is too high to be matched by the bond density of SiO₂. Several structural models have been proposed (1-8) for the SiO₂/Si (100) interface. Most of them assume an atomically abrupt interface. We focus onto the near interface region and study the distribution of intermediate oxidation states (Si¹⁺, Si²⁺, Si³⁺) using core level spectroscopy (9-11). From our data, we can exclude abrupt interface models, since they cannot explain the large portion of Si³⁺ observed at the interface. Recent calculations by Ohdomari, et al. (8) have arrived at an extended interface model for SiO₂/Si(100) by minimizing the strain energy (8). This model is found to be in good agreement with our data. It is not unique, though. A new model is proposed for SiO₂/Si(100) based on the observed distribution and intensity of intermediate oxidation states. Both models are characterized by an extended interface, with protrusions of Si³⁺ reaching about 3Å into the SiO₂ overlayer. In our work, we consider mostly SiO₂/Si interfaces grown in pure O₂, i.e., free of hydrogen or OH. By covering a broad range of oxidation temperatures and pressures we as-
certain that the interface properties hold for a wide class of oxides. The preparation conditions play only a minor role as long as one starts with clean and smooth Si surfaces.

EXPERIMENTAL

Thin SiO$_2$ films were obtained by oxidizing atomically-clean Si surfaces in pure O$_2$. Clean Si(111) 7x7 and Si(100) 2x1 surfaces were prepared by ohmic heating of Si wafers to 1050°C or by dipping in 10% HF and heating to 850°C. Using an ultrahigh vacuum transfer system, the clean Si samples were transferred from the spectrometer (pressure $10^{-10}$ Torr) to a bakeable chamber which could be filled with gases up to a pressure of 1 atmosphere and subsequently pumped down to ultrahigh vacuum. During all oxygen exposures, the sample was cooled while still in oxygen. Thereby, the formation of holes in the SiO$_2$ layer is prevented, which occurs when a thin SiO$_2$ film is heated in vacuum. Vacuum-annealed films with pinholes exhibit a larger signal from bulk Si. The density of Si atoms in intermediate oxidation states is underestimated when using such data.

The experimental technique employed in this work is core level spectroscopy. It has the advantage of resolving the four oxidation states (9,10) of Si via the chemical shift of the Si$_{2p}$ core level. The depth resolution is optimized by using tunable synchrotron radiation. At a photon energy of 130 eV, the escape depth (11) of photoelectrons from the Si$_{2p}$ core level has a minimum of about 7 Å in Si (7 Å in SiO$_2$) compared with about 15 Å (25 Å) in conventional XPS. The short escape depth makes it easy to detect monolayer quantities of Si atoms at the interface. For clarity, all Si$_{2p}$ core level spectra are decomposed into the Si$_{2p_{1/2}}$ and Si$_{2p_{3/2}}$ spin-orbit partner lines using a splitting of 0.60 ± 0.01 eV and the statistical $2p_{1/2}:2p_{3/2}$ intensity ratio of 1:2.

DISTRIBUTION OF OXIDATION STATES

In the Si$_{2p_{3/2}}$ core level spectra shown in Fig. 1, one can clearly identify three peaks between the Si and the SiO$_2$ lines. They are due to intermediate oxidation states, which are labelled Si$^{1+}$, Si$^{2+}$, Si$^{3+}$. One should keep in mind that these symbols refer to the oxidation state, not to the actual charge transfer. The charge transfer is only about half an electrons per oxidation state (9). The energy positions and the widths of the various core lines are given in Table 1. Fig. 1 compares Si$_{2p_{3/2}}$ core level spectra for SiO$_2$ films of different thickness. The intensity distribution of intermediate oxidation states $I^{3+}:I^{2+}:I^{1+}$, does not vary much with the oxide overlayer thickness, showing that this is a universal property of the SiO$_2$ interface. It depends only on the crystallographic orientation of the Si substrate. Si(111) produces less Si$^{2+}$ than Si(100). Results for the intensities obtained from least squares fitting of the data in Fig. 1 are given in Table 1. The intensity of intermediate oxidation states relative to that of the Si substrate (I$^0$) is a measure of their density. It is generally independent of the layer thickness. However, it can be affected both ways by poor sample preparation. Pinholes due to vacuum annealing of thin SiO$_2$ films cause the Si signal to increase. Rough starting surfaces with poor surface core level signals produce more intermediate oxidation states.

Several processing parameters have been varied in order to test the universal nature of the SiO$_2$/Si interface. Pressure and temperature variations (from $10^{-5}$ Torr to 20 Torr and from 700°C to 1100°C resp.) do not affect the distribution of oxidation states significantly. We have also looked into the effect of H$_2$ annealing on the distribution of intermediate oxidation states (Fig. 2). Such annealing is used to reduce the number of interface states in device oxides. There is no noticeable difference. This is understandable since the number of dangling bonds (P$_3$ centers) that can be saturated by hydrogen reaches at most about $10^{14}$cm$^{-2}$ (12) i.e., 1/1000 of a monolayer. Such small changes are not detectable directly with our technique, but the unpinning of the Fermi level can be seen as an overall shift of the spectrum. The presence of H$_2$, e.g. in steam oxidation, has been reported (13) to give rise to