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THE STRUCTURE OF ULTRA-THIN OXIDE ON SILICON

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ABSTRACT

$30\text{\AA}$ thick oxide on silicon has been examined in cross-section by high resolution electron microscopy. The oxide thickness was uniform to within $5\text{\AA}$, even though the oxide undulated with up to $8\text{\AA}$ in height and about $50\text{\AA}$ periodicity.

Ultra-thin ($10\text{-}100\text{\AA}$) silicon oxide layers on silicon are of fundamental interest because they represent the initial stages of silicon oxidation, and of practical importance because of their application in MIS solar cells.⁽¹⁻³⁾ Early studies by ellipsometry,^(2,4-10) XPS^(5,6) Auger spectroscopy,^(7,8) water-droplet contact-angle measurements,⁽⁹⁾ and low and high-energy ion back-scattering^(10,11) have suggested that oxides thinner than about $20\text{\AA}$ are not fully stoichiometric, and that there is a non-stoichiometric transition region of about $20\text{\AA}$ between thicker oxides and silicon. More recent studies of mostly thicker oxides by field dependent photoemission spectroscopy,⁽¹²⁾ medium⁽¹³⁾ and high⁽¹⁴⁾ resolution electron microscopy, ion back-scattering,⁽¹⁵⁾ and Auger^(16,17) and XPS⁽¹⁸⁾ spectroscopies (see Ref. 19 for a review of the recent work) have shown the transition region to be only one or two monolayers wide. An important distinction has also been made⁽¹⁹⁾ between the structural interface (crystal-glass) and the chemical interface (Si-SiO_2). In this paper we report on a high-resolution electron microscopy study (HREM) of the ultra-thin oxides. We show that the structural interface is abrupt, and that the chemical interface is possibly also only one or two monolayers wide.

The ultra-thin oxide was grown on p-type, $1\Omega\text{-cm}$ (100) silicon at 500°C in dry, nitrogen-rich atmosphere, coated with aluminum, and a thin cross-section was prepared by standard methods.⁽²⁰⁾ The cross-section was then imaged at about $3\text{\AA}$ resolution⁽¹⁴⁾ in a 125kV transmission electron microscope with axial illumination at $1400\text{\AA}$ to $1900\text{\AA}$ underfocus. The sample was carefully oriented with the silicon [011] direction parallel to the electron beam, so that the silicon-oxide and oxide-aluminum

interfaces, and the $(11\bar{1})$, $(1\bar{1}1)$, and (200) planes in the crystalline silicon were all resolved edge-on.

The amorphous oxide gave rise to the mottled contrast characteristic of all amorphous materials.⁽²¹⁾ The oxide-aluminum interface was visualized by a Fresnel fringe arising due to the different scattering of the 125kV electrons by the two materials. Subtle and gradual changes in composition that were not accompanied by a marked change of structure or of the average scattering factor, such as a gradual transition between amorphous SiO_2 and amorphous SiO , however, could not be seen.

Fig. 1 shows a medium magnification image of a $2300\text{\AA}$ long section of the ultra-thin oxide. The specimen thickness in the direction normal to the micrograph's plane (direction z) varied fairly linearly from about $100\text{\AA}$ at left to $500\text{\AA}$ at right, as can be deduced from the thickness fringes⁽²²⁾ visible as broad dark bands within the crystalline silicon. The oxide layer is seen to be sharply defined. Its thickness was fairly constant across the whole $2300\text{\AA}$ field, but there was some small ($\approx 3\text{\AA}$ height) undulation of the whole oxide layer with $\approx 300\text{\AA}$ wavelength. This can be seen best in the thin specimen regions at left.

Fig. 2 shows a higher magnification image of the same oxide from a specimen region whose thickness along z varied from about $50\text{\AA}$ at left to about $150\text{\AA}$ at right, where it overlaps with the region shown in Fig. 1. A hill about $8\text{\AA}$ high is now apparent on the Si crystal surface (feature A), and there are several other hills $3\text{--}5\text{\AA}$ high, separated by $30\text{--}60\text{\AA}$. (Alternatively, one could say that there are valleys typically $3\text{--}5\text{\AA}$ and up to $8\text{\AA}$ deep). The actual interface profile was probably slightly rougher than

the profile revealed in this electron micrograph which represents a projection through $50\text{\AA}$ to $150\text{\AA}$ of material along the z -direction. However, since the difference between the roughness seen in $50\text{\AA}$ of material (at left) and $150\text{\AA}$ (at right) is small, the effect of projection was not serious.

Additional information on the interface structure in the z -direction can be obtained from studying the intensity of the lattice plane fringes near the interface. A sharp cut-off of the fringes accompanied by a black-white Fresnel fringe (as at D) indicates that the interface was flat in the z -direction, a gradual fade-out of the fringes (as at C) together with a weak or absent Fresnel fringe indicate roughness along z on a scale comparable to the extent of the fade-out, and isolated patches of lattice fringes extending into the oxide indicate an isolated crystalline protrusion of about the same size as the patch. By far the biggest such patch is at B. It is due to a crystalline protrusion about $10\text{\AA}$ high and $30\text{\AA}$ wide and $20\text{-}30\text{\AA}$ deep. The crystalline protrusion at A, by comparison, is about $8\text{\AA}$ high and $30\text{\AA}$ wide, but considerably deeper than $30\text{\AA}$, since it gives rise to a sharp Fresnel fringe.

The oxide-Al interface is visualized by a white-black Fresnel fringe. It shows undulations which follow closely the silicon-oxide interface undulations, so that the oxide thickness remains constant to within $5\text{\AA}$ (and possibly better) of the average value of $29\pm 3\text{\AA}$, despite the $\approx 8\text{\AA}$ undulations of the silicon-oxide interface. This shows that the oxidation proceeded uniformly across the whole Si crystal, and that the roughness at the silicon-oxide interface originated simply from the initial roughness of the unoxidized silicon.

Compared with previous HREM results on higher temperature, thicker ($1400\text{\AA}$ to several microns) oxides,⁽¹⁴⁾ the present results show stronger short wavelength ($30\text{--}60\text{\AA}$) roughness of the silicon-oxide interface, and slightly weaker longer wavelength ($200\text{--}500\text{\AA}$) undulations. Both types of interfaces, however, exhibit the same abrupt glass-crystal transition.

In order to assess the abruptness of the chemical interface, we performed an independent measurement of the oxide thickness by ellipsometry. The measurement was carried out on the same wafer as used for HREM, but on a part which was only oxidized, and had never been coated with Al. Thickness of $31\pm 3\text{\AA}$ was obtained when the oxide was assumed to be SiO_2 (refractive index $n=1.5$), $27\pm 3\text{\AA}$ for $\text{SiO}_{1.5}$ ($n=1.8$), and $28\pm 3\text{\AA}$ for SiO ($n=2.3$). Although these results are consistent with the $29\text{\AA}$ (HREM value) oxide being fully stoichiometric, the sensitivity of ellipsometry to stoichiometry changes is clearly very limited. Experiments now in progress will measure the absolute oxygen content in the thin oxide and thus hopefully answer the question of oxide stoichiometry with precision limited only by the HREM technique.

In summary, our high resolution electron microscopy of ultra-thin oxides on silicon has shown that: 1) electron microscopy can measure the oxide thickness to $\pm 3\text{\AA}$, independently of the oxide composition, 2) the thickness of the oxide is invariant to within $5\text{\AA}$, even though 3) the oxide undulates with $30\text{--}60\text{\AA}$ periodicity and $3\text{--}8\text{\AA}$ height, 4) the oxide stoichiometry may be determined by comparing the oxide thickness measured by HREM with a measurement of its oxygen content by some other technique, and 5) in the case of ellipsometry, comparison with the HREM results indicates that the $29\text{\AA}$ thick oxide may be fully stoichiometric.

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FIGURE CAPTIONS

Fig. 1 A medium-magnification image of an ultra-thin oxide cross-section.
XBB 799 12255

Fig. 2 A high-magnification image of the same oxide as Fig. 1. The arrows point to individual crystalline silicon protrusions (A,B), and a rough (C) and smoother (D) section of the interface. XBB 790 14708

XBB 796-8466

Fig. 1

Fig. 2