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SiO_2 and Its Interfaces

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SiO_2 and Its Interfaces

Preface

Silicon dioxide is one of the key materials in the microelectronics industry. It is also ubiquitous around us in the form of sand, rocks, glass, as an additive in a variety of products from toothpaste to food, etc. Its properties and those of its interfaces with several materials have long been the subject of extensive research. A number of conferences have been devoted to this research over the years. The Symposium organized at the MRS 1987 Fall Meeting was an attempt to address new results in the field with an emphasis on materials issues. The program covered a broad range of subjects with an interdisciplinary approach. Attendance was very good and discussions were lively. Most papers that were presented at the symposium are included in this volume.

We would like to thank the U.S. Army Research Office for its financial support of the Symposium and Janis Riznychok for her work in putting this volume together.

Sokrates T. Pantelides
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*Invited Paper

THE STRUCTURE OF THE (001)Si/SiO_2 INTERFACE

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ABSTRACT

We show that a careful examination of previous microscopic structural data from the Si/SiO_2 interface reveals that the presence of an epitaxial interfacial oxide cannot be ruled out, and describe the conditions necessary for a definitive search for an intervening layer between c-Si and a-SiO_2. We present electron diffraction and lattice imaging data, which establish the c-Si→a-SiO_2 transition to take place via a crystalline layer ~7 Å thick. Modelling of lattice images in two projections indicates the crystalline oxide to be tridymite, a stable, bulk phase of SiO_2.

INTRODUCTION

The technological dominance of Si is, to a large extent, due to the relative ease with which high quality Si/SiO_2 interfaces can be formed. A variety of pains-taking and ingenious experiments have established the SiO_2 to be stoichiometric and amorphous at distances larger than ~10 Å from the interface. No firm conclusions, however, have been reached regarding the way the perfect structural order in c-Si decays to disorder in a-SiO_2, and how the concomitant chemical change from Si to SiO_2 comes about. These questions are important because, in addition to their technological implications, they address fundamental issues regarding the microscopic mechanism of oxidation, and the structural transition between ordered and disordered states of solids. Attempts to model the Si/SiO_2 interface can be broadly divided into three categories. In the first, the $Si \rightarrow SiO_2$ transition is thought to proceed via an ordered, stable, bulk phase of SiO_2, which bears an epitaxial relationship to the Si substrate. Since cristobalite is obtained by the simple insertion of oxygen atoms between the Si-Si bonds of c-Si, it has been widely suggested as the most likely candidate for an epitaxial oxide. However, although cristobalite is structurally similar to Si, its lattice parameter is 40% larger. An epitaxial relationship between Si and cristobalite is therefore difficult to achieve and results in unrealistically severe bond distortions. The second approach proposes that the $Si \rightarrow SiO_2$ transition is affected through a "substoichiometric" oxide layer, which, although absent from the bulk phase diagram, is nevertheless stabilized by the special conditions existing at the Si/SiO_2 interface. Finally, it has been pointed out that it is structurally feasible to achieve an abrupt transition from c-Si to a-SiO_2 with no intervening layer [1].

Electron diffraction and imaging techniques are in principle ideally suited to the microstructural examination of the Si/SiO_2 interfacial structure, and have indeed been used extensively for this purpose [see e.g. 2,3]. Electron diffraction has produced several indications of the presence of microcrystallites in the oxide, but few firm conclusions regarding the structure or position of these crystallites have been generally reached. Most recently, a systematic study of a variety of Si/SiO_2 samples by grazing incidence X-ray diffraction, using synchrotron sources has provided important new evidence for the presence of microcrystallinity in the Si/SiO_2 system [4]. Diffraction techniques are powerful in revealing the presence of crystallites, but the structural relation of these to the Si substrate and the Si/SiO_2 interface is addressed more directly by imaging techniques.

Transmission Electron Microscopy (TEM), both in the dark-field and the lattice imaging modes, has been used to examine the Si/SiO_2 interface. Dark-field imaging of the Si/SiO_2 interface in plan-view has revealed microcrystallites a few nanometers in size

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[3]. However, these microcrystallites have proved more elusive when the Si/SiO_2 interface has been examined in cross-section in the lattice imaging mode. Thus, while lattice images have been obtained which clearly reveal isolated patches of "oxide" phases at the interface [3], in general the c-Si/a-SiO_2 interface appears abrupt in most lattice images, with no clear indications of an intervening interfacial phase between c-Si and a-SiO_2 [2].

This lack of success in imaging an interfacial phase has been generally interpreted as indicating the absence of an epitaxial oxide phase. A more careful consideration of the bonding requirements at the (100) Si surface does not support this conclusion. The essential point lies in the fact that, although the (100) Si surface is structurally four-fold symmetric, the presence of the Si surface dangling bonds reduce this symmetry to two-fold. In particular, the crossing of a surface step an odd number of atomic layers high causes a 90° rotation in the orientation of the dangling bonds (Fig. 1). An epitaxial interfacial oxide, were it present, would be necessarily tied to these dangling bonds, and would have to rotate through 90° with them on crossing interfacial steps. Thus, unless the interfacial oxide happened to be four-fold symmetric, it would be necessarily polycrystalline, with a grain size determined by the (100) Si surface step spacing prior to oxidation.

Fig. 2 is a schematic representation of the imaging geometry when a Si/SiO_2 interface, with a hypothetical crystalline epitaxial oxide of less than four-fold symmetry, is viewed in cross-section. It is clear that when the spacing between the interfacial steps, and hence the grain size of the oxide are smaller than the sample thickness, the atomic columns in the (poly-) crystalline oxide do not align with each other in projection (Fig. 2). Under these circumstances, lattice images of the interface would show no, or only fleeting indications of the presence of the crystalline oxide. Thus the question of the nature of the c-Si→a-SiO_2 transition can be definitively settled only when the Si surface step spacing, and thus crystalline oxide grains are larger than the typical TEM sample thickness (~100 Å).

In this paper, we show that the examination of Si/SiO_2 samples with sufficiently low interfacial step density directly reveals the presence of a crystalline epitaxial phase at the interface, *both in electron diffraction and lattice imaging.* Matching of experimental and simulated lattice images yields tridymite, a well-known, stable, bulk phase of SiO_2 as the most likely candidate for the observed interfacial phase. We conclude with a brief discussion of the implications of these observations.

EXPERIMENTAL

The samples were produced by growing 2000 Å of Si on a high resistivity (p-type, 2000-3000 Ωcm) (001) Si substrate by Molecular Beam Epitaxy. In-situ RHEED examination of the 2x1 reconstruction, as well as the successful growth of Ge/Si superlattices on the monolayer scale [5], has shown this procedure to produce atomically flat surfaces. The samples were removed from the UHV chamber, and allowed to form a native oxide (~15 Å thick), or annealed in dry oxygen at 700, 800, or 900°C for 30 minutes without the removal of the original native oxide, to form oxide layers up to 180 Å thick. Plan-view samples were prepared by chemical etching from the back and examined in a transmission electron microscope (TEM) operating at 120 kV with the electron beam parallel to the [001] direction, while cross-sectional samples were ion-milled to perforation and examined in a high resolution TEM operating at 400 kV, with the beam parallel to the [110] or [$\bar{1}$10] directions. Simulated lattice images were computed using a standard 128 square array multi-slice program (SHRLI), with a half-empty supercell, 7.68^2 x 27.2 $Å^3$ in