

Direct measurement of the direction of interface motion in the oxidation of metals and covalent solids—Al(111) and Si(100) oxidation with O₂ at 300 K

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Abstract

Four point probe measurements of the surface electrical resistance at an oxide film–metal interface and at an oxide–film semiconductor interface have shown with Å sensitivity that the direction of the buried interface motion during oxide film growth is opposite in the two cases in accordance with the Mott–Cabrera theory. During the formation of amorphous Al₂O₃ layers on Al(111) at 300 K, outward film growth occurs due to Al³⁺ ion transport from the metal into the growing oxide film. For the formation of amorphous SiO₂ layers on Si(100) at 300 K, oxygen transport occurs inwardly into the Si lattice as the oxide film forms.

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1. Introduction

The formation of passive thin oxide films on surfaces of materials provides a natural protection mechanism of great importance in the prevention of metal corrosion [1–4] and for the production of dielectric films needed for semiconductor device fabrication [5,6]. Even though the formation of thin (<30 Å) oxide films has been studied for over 100 years, fundamental questions about the mechanism of oxide film growth still exist, as suggested by the current activity in research on this topic using modern methods of surface science [7–19].

A basic issue concerns the direction of interface motion at the surfaces of metals and covalent solids when a thin oxide film forms. The theory of Mott and Cabrera (MC) [20–22] extending earlier work by Wagner [23], showed that an electric field, naturally produced across a growing thin ionic oxide film, determines the rate of oxidation by controlling the

rate of diffusion of metal cations from the metal to the outer surface of the oxide film. Here metal cations combine with oxide ions. In the framework of this model, oxide film growth should occur in an outward direction from the metallic interface. Electron transfer from the metal to the oxide film, followed by tunneling between electron trap sites in the oxide to the outer surface of the oxide film, provides a counter current to metal ion diffusion through the oxide film during thin film growth [3]. This mechanism explains the observed oxide growth kinetics and the approach to a limiting film thickness in homogeneous oxide thin film growth on metals. The MC mechanism has been modified to some extent to consider inhomogeneous oxide film growth due to nucleation of oxide clusters for some systems [2], and to consider the role of defects on the metal surface [7] and in the oxide film [3,21]. The influence of externally applied electric fields on the rate of oxide film growth on metals supports the MC theory [24]. This large body of knowledge is however not based upon *direct* physical evidence detecting the motion of the metal–oxide interface during oxide film growth.

In contrast to ionic thin film growth, the growth of thin non-ionic oxide films on covalent solids has been postulated to proceed by oxygen penetration into the covalent solid

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[25]. A recent study, involving optical and Auger spectroscopy measurements of oxygen adsorption and oxidation processes on Si(100), suggests that oxidation at the silicon surface occurs initially and is then followed by continued oxidation of silicon in the bulk [15]. Again, these studies do not provide *direct* physical evidence measuring the motion of the semiconductor–oxide interface during oxide film growth.

This paper reports high sensitivity electrical measurements of the motion of the interface between substrate atoms and the oxide film formed on a metallic and on a covalently bonded solid. Both solids are known to produce homogeneous oxide films beyond monolayer oxidation [19,26]. We employ a special ultrahigh vacuum four-point probe *scanning tunneling microscope (STM)* apparatus [27]. Here four independently movable STM tips are used to make current/voltage measurements of surface resistivity over a lateral (x,y) distance, d (between the inner probes) of 300 nm. The apparatus allows the surface of the solid to be located in the z coordinate to Å accuracy using the STM feedback prior to electrical contact before and during oxidation. The measurements show that Al(111), during oxidation by $O_2(g)$ at 300 K, retains its metallic conductivity at the interface position, whereas Si(100) becomes less conductive. The measurements directly show therefore that the oxidation of a representative metal, Al, occurs by outward growth of the oxide film from the initial surface location. In contrast, the oxidation of a non-metal, silicon, takes place by inward motion of the buried interface. The difference between outward film growth (ionic oxide) and inward film growth (non-ionic oxide) is schematically shown in Fig. 1a and b.

2. Experimental details

The experiments were conducted in an ultrahigh vacuum (UHV) system operating at a base pressure of 4×10^{-8} Pa [27]. The UHV-system is composed of chambers interconnected with each other via a transfer system: (1) a load-lock chamber for fast entry of samples and probes; (2) a chemical preparation and analysis chamber equipped with standard surface science tools such as *Auger Electron Spectroscopy (AES)*, *Low Energy Electron Diffraction*, *X-ray Photoelectron Spectroscopy*, *Quadrupole Mass Spectrometry* and a gas handling system; and (3) a unique chamber combining four STM probes which are imaged with a scanning electron microscope for four-point-probe conductivity measurements at sub-micrometer tip separation. As shown in Fig. 1c, the STM stage is suspended on springs and is further isolated from external vibrations via an eddy-current damping system. In addition, the entire UHV system rests on an active vibration isolation system. The four nanomanipulators, oriented at 45° from the normal, and at 90° from each other, electrically probe a small region on the surface of a material of interest. They are guided by a scanning electron microscope (SEM) which images both the surface and the probes as shown in Fig. 1d. It should be noted that the nanomanipulators are controlled independently from each other. Four-point-probe conductivity measurements are performed in the following way: once the atomically clean sample is transferred to the STM/SEM chamber, all four probes are caused to approach the surface using the STM feedback loop control. The SEM is used to guide the probes with respect to each other and to determine the spacing between the probes. Once all four tips are in tunneling contact, the tunneling current

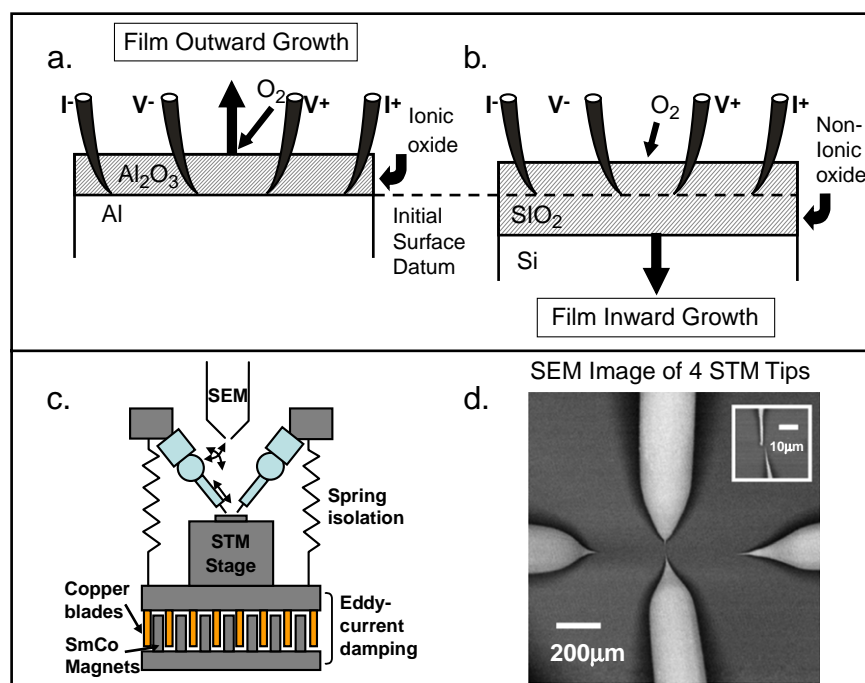


Fig. 1. Schematic of electrical measurement of oxide film growth direction on (a) Al(111) and (b) Si(100) crystals. (c) Schematic of the multiple tip STM–SEM chamber for electrical measurements. The STM stage is suspended on springs and is further vibrationally isolated via an eddy-current damping system; (d) SEM image of the 4 STM probes during approach to the Si(100) crystal surface.

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