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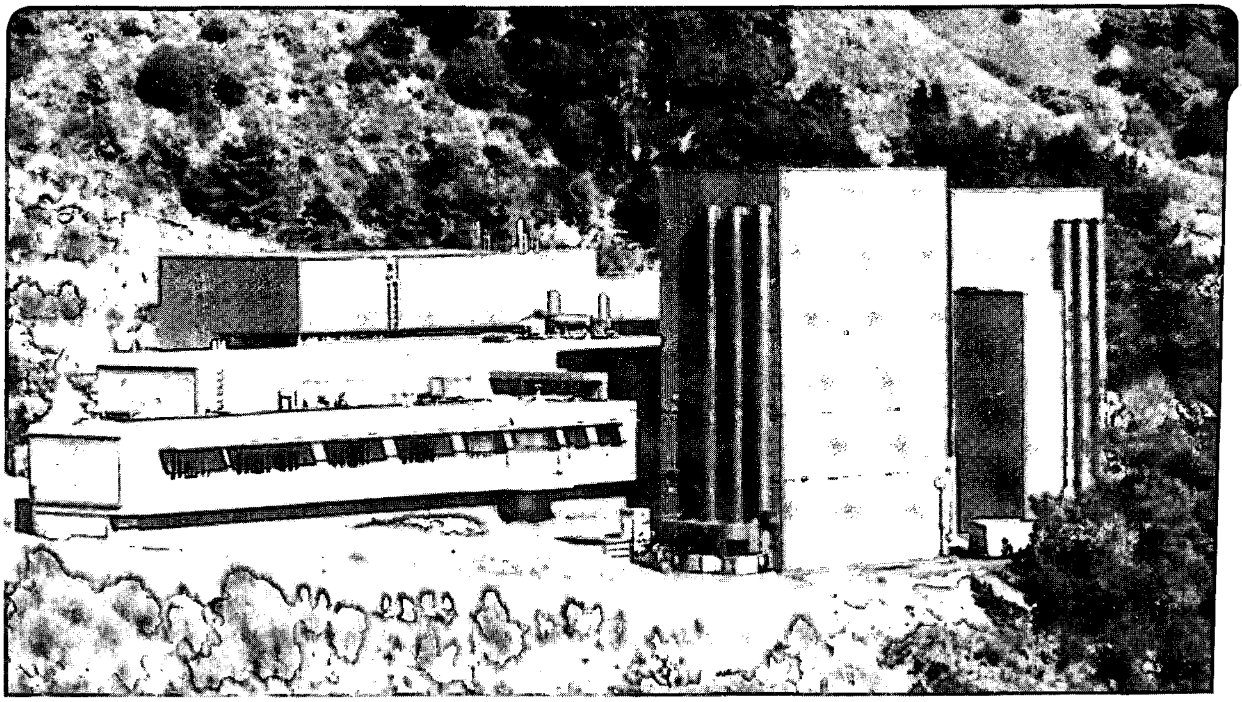

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STRUCTURAL AND INTERFACIAL CHARACTERISTICS OF THIN (<10 nm) SiO_2 FILMS GROWN BY ELECTRON CYCLOTRON RESONANCE PLASMA OXIDATION ON [100] Si SUBSTRATES

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ABSTRACT

The feasibility of fabricating ultra-thin SiO_2 films on the order of a few nanometer thickness has been demonstrated. SiO_2 thin films of approximately 7 nm thickness have been produced by ion flux-controlled Electron Cyclotron Resonance plasma oxidation at low temperature on [100] Si substrates, in reproducible fashion. Electrical measurements of these films indicate that they have characteristics comparable to those of thermally grown oxides. The thickness of the films was determined by ellipsometry, and further confirmed by cross-sectional High-Resolution Transmission Electron Microscopy. Comparison between the ECR and the thermal oxide films shows that the ECR films are uniform and continuous over at least a few microns in lateral direction, similar to the thermal oxide films grown at comparable thickness. In addition, HRTEM images reveal a thin (1-1.5 nm) crystalline interfacial layer between the ECR film and the [100] substrate. Thinner oxide films of approximately 5 nm thickness have also been attemped, but so far have resulted in nonuniform coverage. Reproducibility at this thickness is difficult to achieve.

INTRODUCTION

The need for low temperature thin film processing techniques has become increasingly important as the dimension of the integrated devices continues to decrease.

Silicon dioxide is a key element in many solid state devices, in particular the metal - oxide - semiconductor (MOS) field effect transistor. It can serve as the gate dielectric material or as an insulator between adjacent transistors and metal interconnections. The oxides have been traditionally grown by thermal dry oxidation at temperature above 1100°K and have high electrical and physicochemical properties.[1] Processing at such high temperature, however, can have undesirable side effects, such as enhanced silicon defect formation, redistribution of dopant profiles via solid-state diffusion, and wafer deformation upon cooling due to residual stress in the films grown.[2] As a possible alternative, Electron Cyclotron Resonance (ECR) plasma oxidation at temperature below 700°K can provide oxides with physical characteristics identical to thermal oxides, and electrical properties acceptable for device manufacture and approaching those of thermal oxides.[3]

To achieve these high electrical characteristics, the thin oxide films however must show uniform and continuous in thickness through an extended lateral dimension. As the film thickness decreases, the interfacial structure between the amorphous SiO_2 and the Si substrate also becomes more critical in determining the electrical properties. Hence, understanding and characterization of the structural characteristics of the thin oxide films and at the Si/SiO_2 interface are of critical important in semiconductor technology. Most studies of interfacial structure at this interface have employed the High-Resolution Transmission Electron Microscopy (HRTEM) and related methods, which provide lattice imaging of the structure at an atomic scale.[4-11] Thermal oxide interfaces were shown to be quite uniform and had a roughness of 1-2 atomic planes.[5-8,12] Fresnel analysis of HRTEM images revealed the presence of a layer of intermediate composition SiO_x in the order of a few nanometer.[8] Existence of a thin microcrystalline phase of SiO_2 at the interface has also been reported recently.[9,13] From observation of TEM[9] and X-ray scattering,[13] the new phase was infered to be of tridymite or cristobalite structure. Calculations of the atomic and electronic structures of $[100]Si/SiO_2$ interfaces by empirical tight-binding method,[14] by first-principles total energy band-structure calculations within the local-density-functional formalism,[15] and by molecular volume argument which reduces excess free energy storage[16] indicated that cristobalite SiO_2 is the most plausible structure. The authors in the first two calculation methods examined the connection between the Si substrate and the cristobalite SiO_2 phase in the amorphous oxide layer through minimum lattice mismatch,[14,15] while the author in reference 16 proposed that Si crystal is transformed into crystobalite SiO_2 plus interstitial Si atoms in the oxidation process.

In this paper, we report the electrical data of thin SiO_2 films grown by Electron Cyclotron Resonance plasma oxidation on [100] Si substrates and present a structural studies of the films and their Si/SiO_2 interfaces by High-Resolution Transmission Electron Microsopy.

EXPERIMENTAL TECHNIQUES

The apparatus and procedures for growing oxide films in an ECR chamber have been described in detail elsewhere.[3,17] The reactor employed a 2.45 GHz, 800 W CW microwave power supply/matching network, and electromagnets driven in mirror configuration to establish the axial magnetic field. A single two or three-inch Si wafer, located 14 cm away from the source chamber, can be deposited at a time. Before growing the film, the substrate was heated to the desired temperature under a pressure of approximately 10^{-4} Pa. Oxide film thickness was measured initially using ellipsometry. Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectrocsopy (AES), and oxide etch rates in 5:1 buffered oxide etchant (BOE) were used to charaterize the physical and chemical properties of the oxides. Electrical data were obtained from MOS capacitor structures fabricated by thermal evaporation of aluminum or n^+ polysilicon on the oxides.

To study the structural properties of the ECR oxides, aluminum rather than polysilicon overlayers were deposited on top of the oxide layers, at temperature comparable to that during ECR processing, to retain the microstructures of the films and the interfaces grown by this low temperature method. Cross-sectional samples for TEM observation were prepared by mechanical thinning to approximately 30 μm, followed by ion beam milling in a cold stage at 5 kV.[18] The samples were studied in a JEOL JEM 200CX electron microscope, equipped with a high resolution goniometer, operating at 200 kV. The films were imaged with the electron beam parallel to the [110] of the Si substrate.

RESULTS AND DISCUSSIONS

Physical, Chemical, and Electrical Measurements

Analysis of physical, chemical, and electrical properties of the ECR oxide films have been reported earlier.[3] The physical and chemical characteristics of the as-grown oxides of 60 nm or less thickness were identical to those of the thermal oxides grown at 1123°K or higher in temperature. The refractive index and etch rates in BOE solutions were identical to those in dry thermal oxides. FTIR, XPS, and AES spectra revealed no observable chemical differences between the ECR oxides and the thermal oxides. High frequency capacitance - voltage (C-V) and ramped bias current current - voltage (I-V) studies performed on 5.4 to 30 nm thick capacitors indicated that the as-grown ECR films had high levels of fixed oxide charge ($> 10^{11}$ cm^{-2}) and interfacial traps ($>10^{12}$ cm^{-2} eV^{-1}), although these values can be reduced by a 20 minute polysilicon gate activation anneal at 1123°K in nitrogen. The mean breakdown strength for oxides grown under optimum conditions was 10.87 ±0.83 MV cm^{-1}. Electrical properties of the 5.4 to 8 nm gates compared well with thicker films and with dry thermal oxides of similar thicknesses.

Structural characterization

HRTEM was used to compare ECR oxides to thermal oxides of equivalent thicknesses. Figure 1 shows images of thick ECR and thermal oxide films, capped with an evaporated aluminum gate, grown on Si substrates. The thickness of the ECR oxide in figure 1a) is approximately 100 nm, and of the thermal oxide in figure 1b) is about 70 nm. At this magnification, both oxides seem to show uniform film thickness and interfaces. Both the Si/SiO_2 interfaces and the oxide - aluminum interfaces are flat over an extended area. The structures of two oxides are indistinguishable from each other.

General observation of the Si/SiO_2 interfaces of oxides grown thermally and in ECR plasma reactor revealed no significant differences in structure and roughness. Figures 2a) and b) show images of the Si [100] substrate - oxide interface of the thermal oxides and ECR oxides, respectively. Both images indicate that the roughness at the interface is within a few atomic planes. They also show that the interface between the ECR oxide and the Si substrate is atomically flatter than that between the thermal oxide and the Si substrate. No conclusive evidence for the presence of a SiO_x layer or a new phase can be obtained from observation of these TEM images alone.

Thin oxide films of 7 nm thickness have been produced by this fabrication method in reproducible fashion. Cross-sectional images of such a thin oxide with an aluminum overlayer and the corresponding diffraction pattern are shown in figure 3. The thickness of the film is uniform over the region that is visible in the electron microscope, which is at least a few micron long, as can be seen in figure 3a). Figure 3b) shows a high magnification of a smaller region from figure 3a). No defects or pores are apparent in the film. The interface between the oxide layer and the aluminum overlayer appears perfectly sharp in the image, although it is a result of Fresnel fringe effects at a large positive defocus value.[19] The Si/SiO_2 interface seems flat to within 1-2 atomic planes. A transition layer of thickness 1-1.5 nm between the ECR oxide and the [100] Si substrate shows a new crystalline phase that is different from the structure in the bulk substrate. This crystalline interfacial layer can be seen more clearly in a magnified image shown in figure 4. The atomic plane between the arrows indicates the boundary between the new crystalline phase and the bulk Si [100]. Although the structure of this new phase cannot be determined from the TEM image, it may be a crystalline SiO2 layer that results from transformation of the Si lattices, as suggested in the model by Tiller.[16] Further analysis, including processing and matching of the image with computer simulation, is required to determine this feature.

Attempt at forming thinner oxide films of approximately 5 nm thickness have resulted in nonuniform coverage. The thickness of the film varies from 4 to 6 nm and reproducibility is not easily achieved. Further studies of oxide growth kinetics are required if oxide films of this thickness are desired.

CONCLUSIONS

Oxide thin films of thickness less than 10 nm and thicker have been successfully fabricated at low temperature by Electron Cyclotron Resonance plasma oxidation method. The physical characteristics of these films are identical to those of thermal oxides of the same thickness. The electrical properties are acceptable for device manufacturing and approach those of thermal oxides. Cross-sectional TEM indicates that the ECR films are uniform and continuous over a large area, similar to the thermal oxides of comparable thicknesses. HRTEM also reveals the presence of a thin (1-1.5 nm) crystalline interfacial layer that is distinct from the bulk Si between the ECR oxide and the Si [100] substrate in a 7 nm thick oxide sample. Attempts of fabricating oxides of thickness 5 nm by ECR had resulted in films of continuous but nonuniform thickness.

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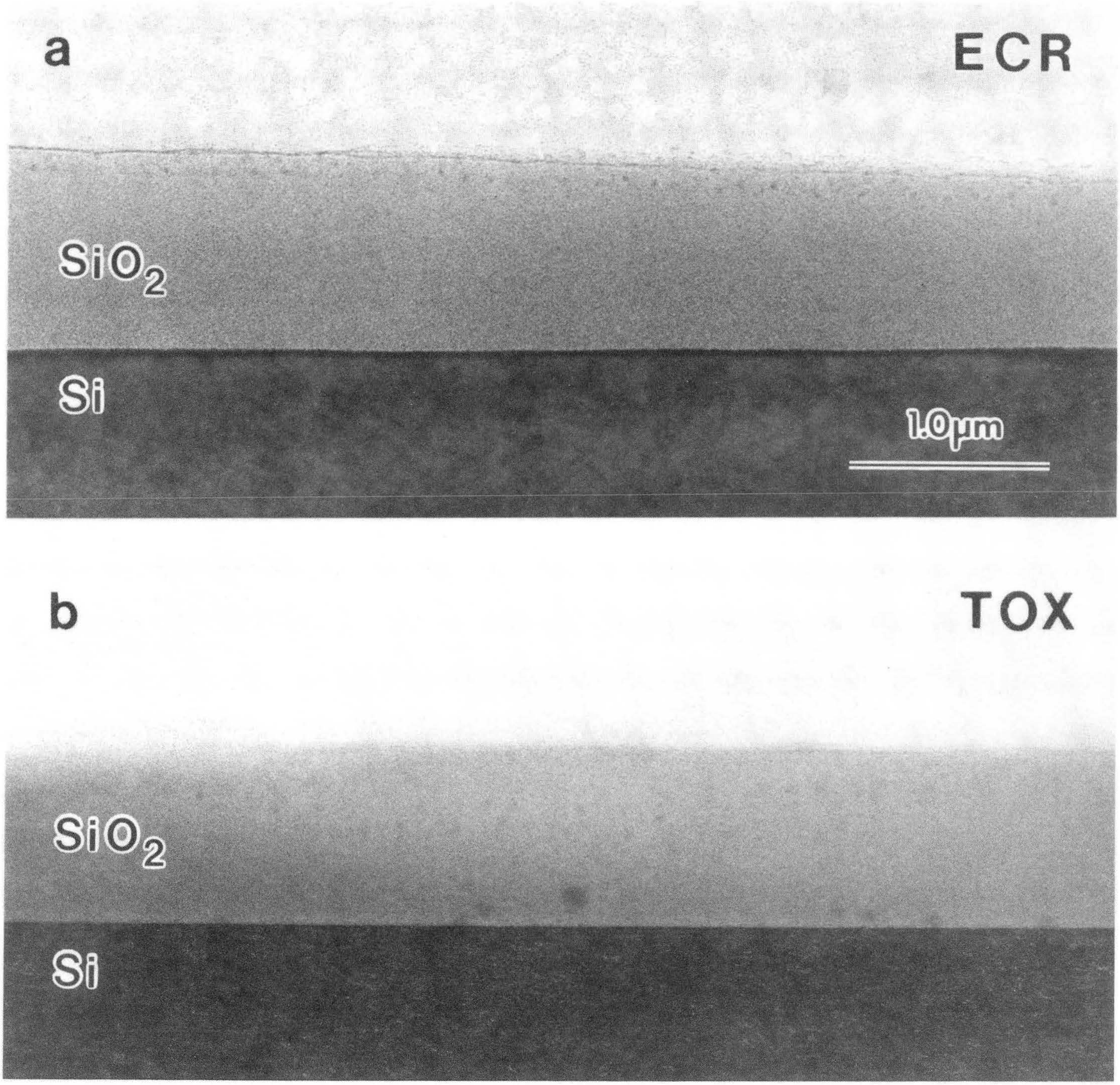

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Figure 1.-- Cross-sectional TEM images of a) 100 nm ECR oxide, and b) 70 nm thermal oxide films grown on Si substrates. They show similar film uniformity and interfaces over large areas.

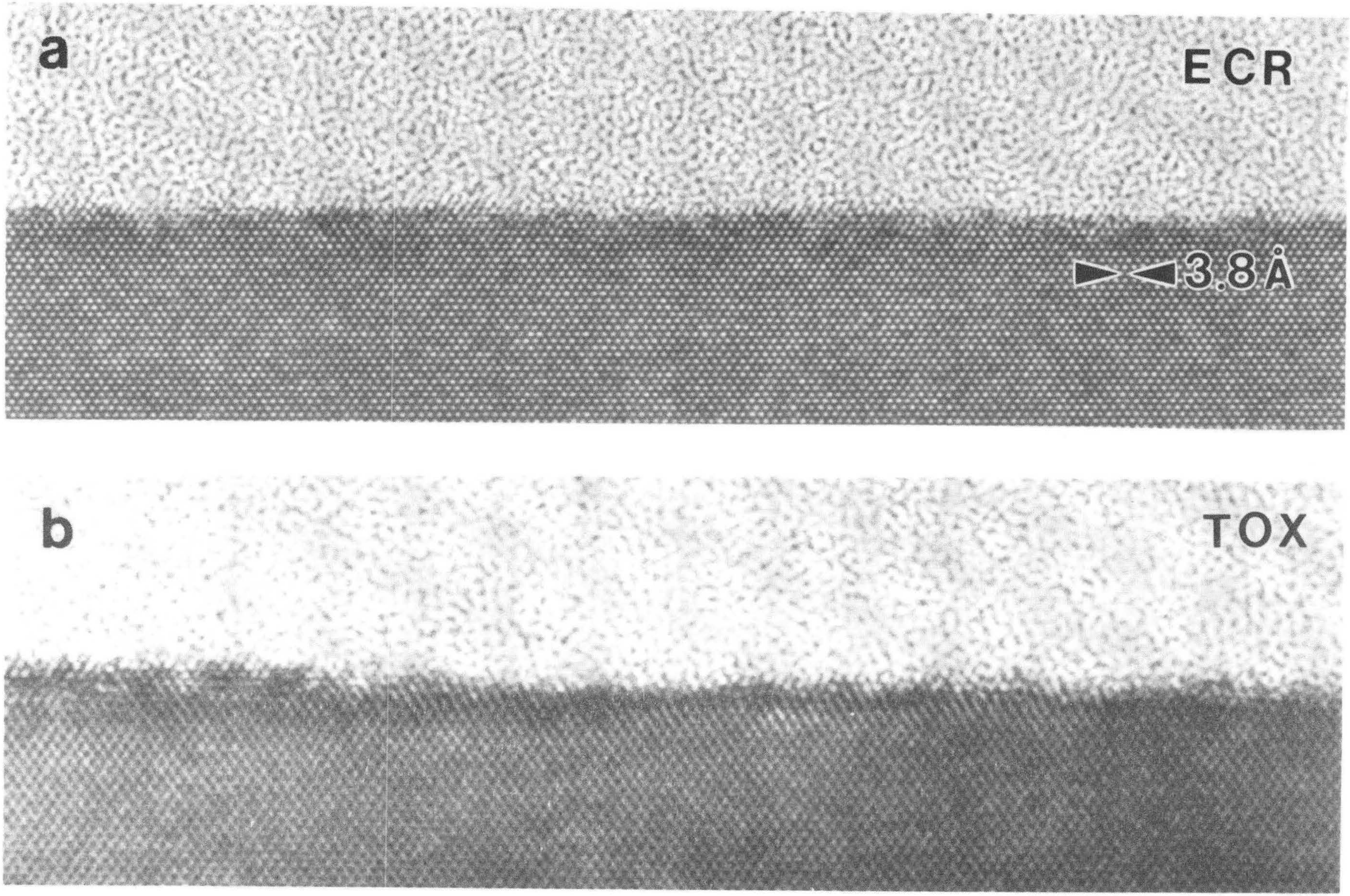

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Figure 2. -- HRTEM images of Si/SiO_2 interfaces of a) ECR oxide and b) thermal oxide films grown on [100] Si substrates. The interface in the ECR film appears more atomically flat, and both images indicate an interfacial roughness of a few atomic layers.

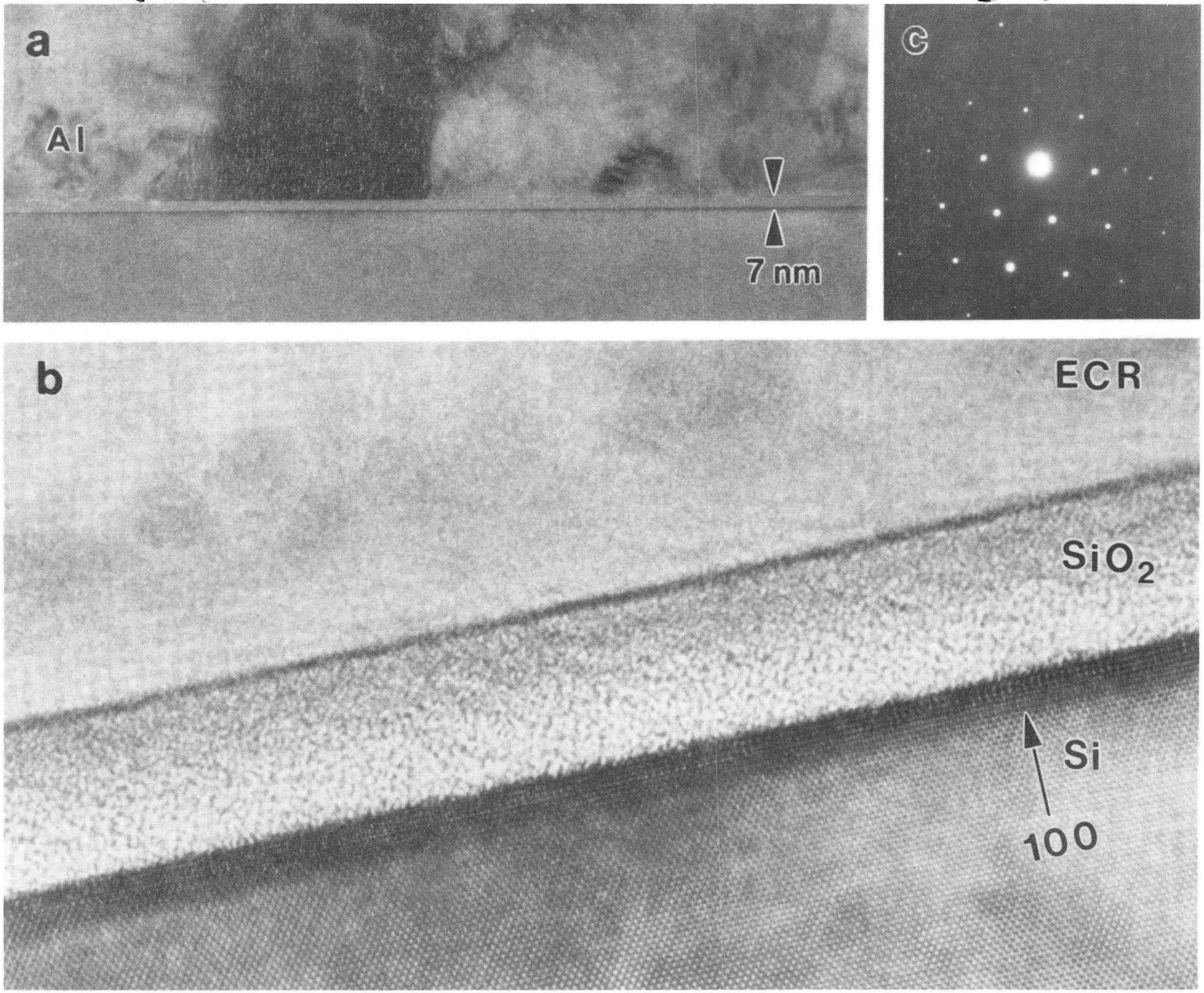

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Figure 3. -- Images of a 7 nm thick ECR oxide film grown on [100] Si substrate with an aluminum overlayer. a) Low magnification shows uniform thickness over long distances, b) high magnification of a region in a), and c) electron diffraction pattern showing the spots from the Si substrate.

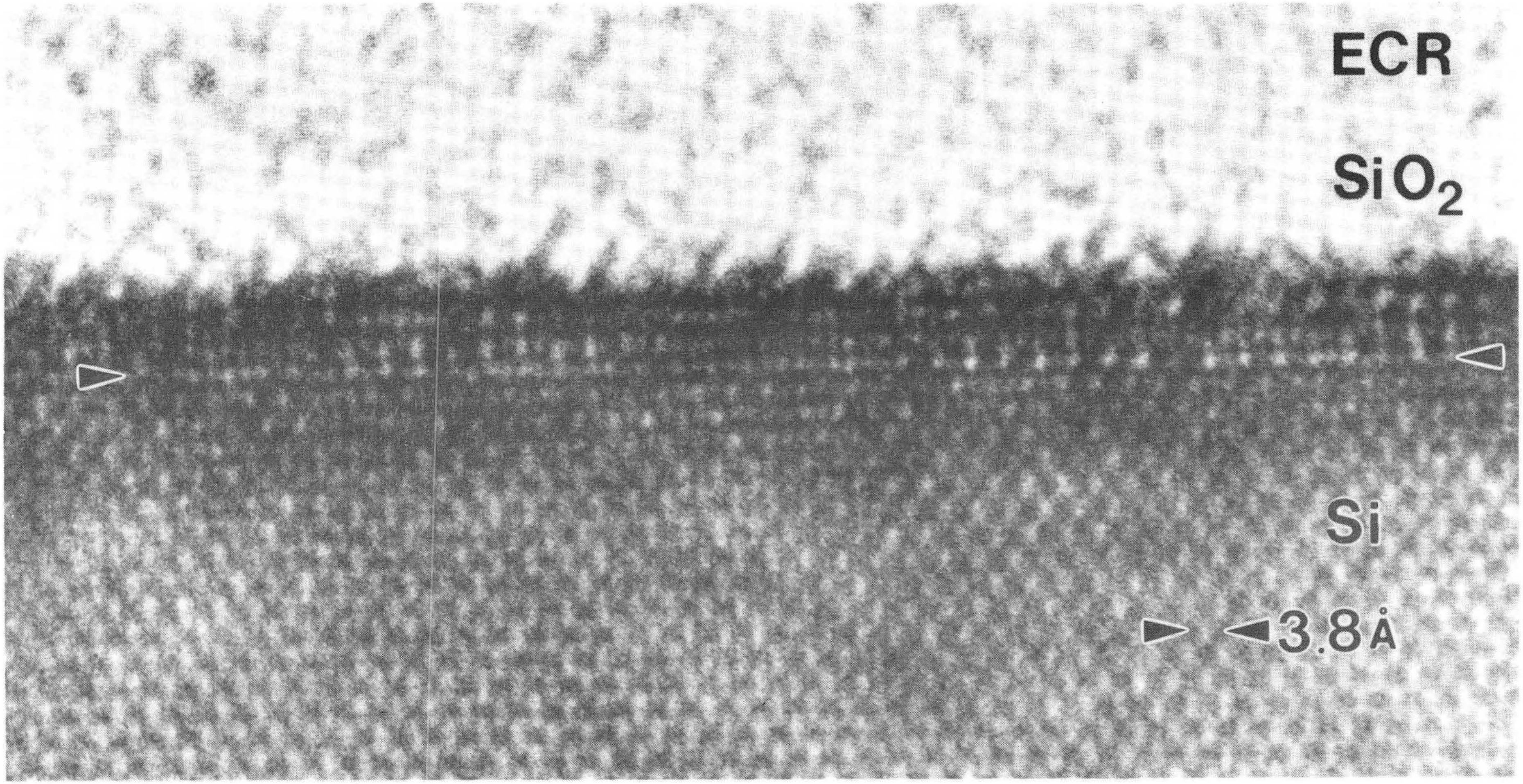

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Figure 4. -- High magnification image of the 7 nm ECR oxide film in figure 3, showing the thin (1-1.5 nm) crystalline interfacial layer between the oxide and the [100] Si substrate.