New approach to the preparation of ultrathin silicon dioxide films at low temperatures

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(Received 9 March 1992; accepted for publication 1 June 1992)

Ultrathin silicon dioxide films have been prepared on a Mo(110) substrate at a relatively low temperature (< 100 °C) by evaporating silicon in an oxygen background. The SiO₂ films were characterized by Auger electron, electron energy loss, and IR reflection absorption spectroscopies. At low substrate temperatures, the SiO₂ films are amorphous, consisting of networks of [SiO₄] tetrahedra units with limited size. Upon post-annealing, the small networks of [SiO₄] fuse together, and become more ordered. In turn, the electronic properties of the SiO₂ films approach those of vitreous silica.

There is a growing interest in the synthesis of thin silicon dioxide films at low substrate temperatures for microelectronic processing.¹,² High quality silicon dioxide films are utilized as interlayers for multilevel metallization, as passivation layers and as the active insulating material in metal-oxide-semiconductor structures. Low-temperature processing is desirable in all of these applications in order to prevent device degradation. A number of approaches have been used to produce films at low substrate temperatures, for example, chemical vapor deposition (CVD),³ plasma enhanced CVD,⁴ and laser induced CVD.⁵ However, films prepared with these methods typically contain impurities such as hydrogen or nitrogen, depending on the particular precursors used.

In this letter, we report a novel and simple method to prepare very pure and stoichiometric SiO₂ thin films at low temperatures (< 100 °C). A thin film of silicon dioxide is prepared on a Mo(110) substrate by evaporating silicon in an oxygen background. A Mo(110) single crystal was chosen as the substrate because of its relative ease of cleaning and the ability to thermally desorb the thin films of SiO₂ from the surface.

Experiments were performed in two ultrahigh vacuum chambers. One chamber is equipped with a Perkin-Elmer double pass CMA used for Auger electron spectroscopy (AES) and electron energy loss spectroscopy (ELS). The other chamber is equipped with a Mattson Cygnus 100 FTIR spectrometer for infrared reflection absorption spectroscopic (IRAS) studies. The Mo(110) substrate was cleaned by heating in oxygen at 1200 K and flashing to 2200 K in vacuo. The substrate was positioned ~1 in. away from the silicon source which was constructed by wrapping a small piece (~1 x 1 x 3 mm) of silicon (from a high-purity silicon wafer) with a tantalum heating wire. By resistively heating the tantalum wire, high-purity silicon can be evaporated onto the Mo(110) substrate under ultrahigh vacuum conditions. The purity of the silicon films (< 1 at. %) is evident in the Auger spectra of Fig. 1(a).

Silicon dioxide is formed on the substrate at room temperature when silicon is evaporated in a ~ 4 x 10⁻⁶ Torr O₂ background. Figure 1 shows the Auger electron spectra for the films prepared under oxygen background pressures of 0 (spectrum A), 1 x 10⁻⁶ (spectrum B), and 4 x 10⁻⁶ Torr (spectrum C). Silicon and silicon dioxide species are differentiated based on their characteristic Auger transition energies and line shapes. Silicon dioxide has characteristic LVV Auger transitions at 76, 63, and 59 eV, whereas silicon has a major Si(LVV) peak at 91 eV.⁶,⁷ In addition, an AES feature at ~ 85 eV has been observed for the SiO species on platinum⁸ and on silicon.⁹ Clearly, both silicon and silicon dioxide are evident in the intermediate oxygen pressure range of 1 x 10⁻⁶ Torr. The Auger line shapes and the relative intensities of the silicon and oxygen features remain unchanged for films prepared at oxygen pressure greater than ~ 4 x 10⁻⁶ Torr, consistent with the production of only a silicon dioxide film at the higher oxygen pressure conditions.

The ratios of the silicon and oxygen AES features in the spectra shown in Fig. 1 further suggest that the silicon oxide films are stoichiometric, i.e., SiO₂. The presence of SiO (silicon monoxide) in the silicon oxide films can be ruled out on the basis of the absence of an Auger transition at ~ 85 eV.⁸,⁹ Other silicon-oxygen species, such as Si₂O and Si₃O₂, are not likely to be formed, since these species do not exist as stable compounds; these species have only been proposed to exist at the Si/SiO₂ interface.¹⁰,¹¹ Furthermore, the line shapes, the peak energies of the Auger electrons, and the electron energy loss spectra (Fig. 2) are consistent with those of silicon dioxide.

Figure 2 shows the first-derivative electron energy loss spectra of the silicon dioxide films annealed to various temperatures. Vitreous silicon dioxide exhibits optical excitations at 10.3, 11.8, 14.0, 17.0, and 22–23 eV.¹² In addition, electron energy loss features at 10, 12, 14, 17, 20, and 23 eV have also been reported for thermally grown silicon dioxide on a silicon substrate.¹³–¹⁶ These electron energy loss features are attributed to interband transitions¹⁵,¹⁶ whereas the 23 eV feature is assigned to a bulk plasmon excitation.¹⁶

The electron energy loss spectrum for the silicon dioxide films on Mo(110) after annealing to 900°C displays features identical to those of vitreous silica, i.e., features at ~ 10, 12, 14, 17, and 20 eV. The silicon oxide films pre-
pared at room temperature exhibit additional low energy electron loss features at ~5 and 7 eV. These features are attributed to a local structure with broken Si—O bonds in tetrahedra of [SiO₄]. Defect-free vitreous silica consists of [SiO₄] tetrahedra connected by an oxygen bridge to form a long range 3D network. Thus the ~5 and 7 eV EELS features indicate the presence of smaller [SiO₄] networks. The EELS features at 5 and 7 eV have previously been observed for silicon oxide films prepared by thermally oxidizing a silicon wafer. The intensity of the electron energy loss features at 5 and 7 eV is significantly decreased upon heating, and completely disappears after annealing to 900 °C. This behavior suggests that the silicon dioxide films undergo structural reorganization, eliminating the local structure with broken Si—O bonds, to form a long range 3D network of [SiO₄].

The IRAS data provide additional information regarding the structural changes that occur when the silicon di-

oxide films are annealed (Fig. 3). The asymmetric stretch motion of the Si—O bonds appears as a broad asymmetric peak centered at 1178 cm⁻¹ in the IRAS spectrum for the film prepared at a substrate temperature of 50 °C. This peak gradually shifts to higher frequency upon heating the film, reaching a maximum of 1252 cm⁻¹ for the film annealed to 1200 °C. The features associated with the symmetric stretching (~810 cm⁻¹) and rocking (~460 cm⁻¹) vibrational modes for vitreous silica were not accessible in this study due to the cutoff of the CaF₂ windows.

The IRAS spectra for the silicon dioxide films on the Mo(110) substrate are significantly different from those obtained using transmission IR absorption in the 1000-1300 cm⁻¹ region. These differences can be attributed to the so-called Berreman effect. Accordingly, the transmission IR absorption spectra for fused quartz and silicon dioxide films exhibit a strong adsorption peak at 1076 cm⁻¹ with a higher wave number shoulder extending to 1300 cm⁻¹. In contrast, the IRAS spectra for the silicon dioxide films do not have features at 1076 cm⁻¹. The spectra, in fact, are dominated by features above 1200 cm⁻¹. Two vibrational oscillators of asymmetric stretches (AS₁ with in-phase motion of adjacent oxygen atoms and AS₂ with out-phase motion of adjacent oxygen atoms) of silica are present in this wave number regime. The transverse-optical (TO) and longitudinal-optical (LO) vibration modes are at 1076 cm⁻¹ (TO) and 1256 cm⁻¹ (LO), for AS₁, and at 1200 cm⁻¹ (TO) and 1160 cm⁻¹.
The TO modes are optically active whereas the LO modes are optically inactive for an infinite crystal. These selection rules arise because the electromagnetic waves are transverse, and thus do not interact with the longitudinal phonons. However, for thin films with thickness much smaller than the wavelength of the lattice vibration, the vibrational modes normal to the surface have the frequencies of the longitudinal modes. For the vibrational modes parallel to the surface the frequencies correspond to the transverse modes. Since only the vibrational modes with a component normal to the metal surface are IR active, the IRAS spectra for the silicon dioxide films exhibit only these features corresponding to the longitudinal modes. Thus the spectra from the films should differ from the corresponding spectra taken with transmission IR absorption that mainly probes the transverse features.

The increase of the peak IRAS frequency with the annealing temperature for silicon dioxide films on Mo(110) (Fig. 3) suggests some ordering of the SiO$_2$ film upon heating. The broad peak in the IRAS spectra for the SiO$_2$ films is attributed mainly to a convolution of the longitudinal optical modes of the asymmetric stretches of AS$_1$ (1256 cm$^{-1}$) and AS$_2$ (1160 cm$^{-1}$) of silicon dioxide. These two modes are coupled via disorder in the SiO$_2$ films. The AS$_2$ mode is optically weak in crystalline a quartz and its intensity increases with a concomitant decrease of the AS$_1$ intensity in amorphous silicon dioxide. Therefore, the increase of the intensity at 1250 cm$^{-1}$ and the decrease of the intensity at 1160 cm$^{-1}$ strongly indicate that the SiO$_2$ film becomes more ordered with heating. This is also consistent with the EELS results.

The SiO$_2$ films are prepared in an ultrapure oxygen environment ($\sim 10^{-5}$ Torr) and do not contain impurities such as carbon and hydrogen within AES and IRAS detectable limits. IRAS does not show any features at 3650 and 2300 cm$^{-1}$, characteristic of OH and Si-H stretches, and is consistent with very low background partial pressures of water.

In conclusion we have shown that thin, stoichiometric silicon dioxide films can be grown on a Mo(110) substrate at relatively low temperatures by evaporating silicon in an oxygen background. The silicon dioxide films prepared at these low substrate temperatures are amorphous and contain some short-range networks of SiO$_4$ tetrahedra units. During post-annealing, the films become more ordered and consist of long range [SiO$_4$] networks. The silicon dioxide thin films prepared by the present method are of very high purity compared to other methods, such as CVD, plasma enhanced or laser induced CVD. In addition, the deposition rate can be accurately controlled, in contrast to thermal oxidation. Therefore, this method of depositing SiO$_2$ thin films may be applicable to some microelectronic processing where low substrate temperatures, high purities, and precise film thicknesses are required.

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.