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Embedded structure of silicon monoxide in SiO_2 films

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Abstract

The structure of SiO_x (x = 1.94) films has been investigated using both X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The SiO_x films were deposited by vacuum evaporation. XPS spectra show that $SiO_{1.94}$ films are composed of silicon suboxides and the SiO_2 matrix. Silicon clusters appeared only negligibly in the films in the XPS spectra. Si_3O^+ ion species were found in the TOF-SIMS spectra with strong intensity. These results reveal the structure of the films to be silicon monoxide embedded in SiO_2, and this structure most likely exists as a predominant form of Si_3O_4. The existence of Si–Si structures in the SiO_2 matrix will give rise to dense parts in loose glass networks.

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Keywords: SiO_x films; Silicon suboxides; X-ray photoelectron spectroscopy; Secondary ion species; Time-of-flight secondary ion mass spectrometry

1. Introduction

SiO_x films are well known and extensively studied materials [1–6] that are very attractive for applications as dielectrics [7,8] and transparent gas barrier films [9,10]. In particular, additional interest in these materials has arisen out of curiosity in their structure in the nanoscale due to the non-stoichiometric silicon oxides [11–14].

Silica glass is thought to be comprised of a randomly networked-structure of Si–O bonds with four-coordination number of silicon atoms surrounded by oxygen atoms and linked to other units through Si–O–Si bridges [1,6]. Although the ratio of silicon to oxygen atoms is 2.0 for the most-energetically stable, that is, fully-oxidized and stoichiometric silicon oxide, thin film compositions with ratios less than 2.0 are frequently used for applications in electronics [7] and optics [8]. These have the composition SiO_x [1–6], wherein x is in the range $0 < x < 2$. Due to excess silicon atoms producing optical absorption in the visible range, compositions with x close to 2.0 are preferable in order to attain transparency. For instance, thin films with x between 1.9 and 2.0 have been used as transparent gas barrier films [9,10]. In the Si–SiO_2 phase diagram, the intermediate oxidation states of silicon cannot be identified; it is not clear that silicon monoxide exists in the phase diagram [1,15,16]. There is also significant curiosity and interest in the structure of SiO_x films, in particular, transparent SiO_x films in the nanoscale.

Secondary ion species in time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra could play a powerful role in providing information on solid structures in the nanoscale [17,18]. $SiO_{1.94}$ films were investigated in this study using TOF-SIMS spectra in association with peak analysis in X-ray photoelectron spectroscopy (XPS) spectra [17,19].

2. Experimental

Two types of samples were used in this study: 25 nm-thick SiO_2 films and 94 nm-thick SiO_x films. 25 nm-thick thermally-oxidized as well as plasma-enhanced CVD-prepared SiO_2 films on single-crystal n-type (1 0 0) silicon wafers (resistivity of 4–6 Ω cm) were received from Tohoku Semiconductor Co. SiO_x films with 94-nm thickness were deposited onto poly-(ethylene terephthalate) (PET) films at room temperature using electron beam evaporation of a mixture of silicon and silicon dioxide. The vacuum pressure was 5.0×10^{-3} Pa. The atomic

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composition x of the films was determined by XPS and was shown to be 1.94 ± 0.03.

XPS measurements were performed using an ULVAC-PHI Quantera SXM spectrometer with an Al Kα X-ray source. Sputter etching was accomplished using either Ar^+ ions at 500 V or C_{60}^+ ions at 10 kV rastered over a 2 mm × 2 mm area. This corresponds to an etching rate of about 0.02 nm/s for the SiO_2 films. For the C_{60}^+ ion source, a differentially pumped C_{60}

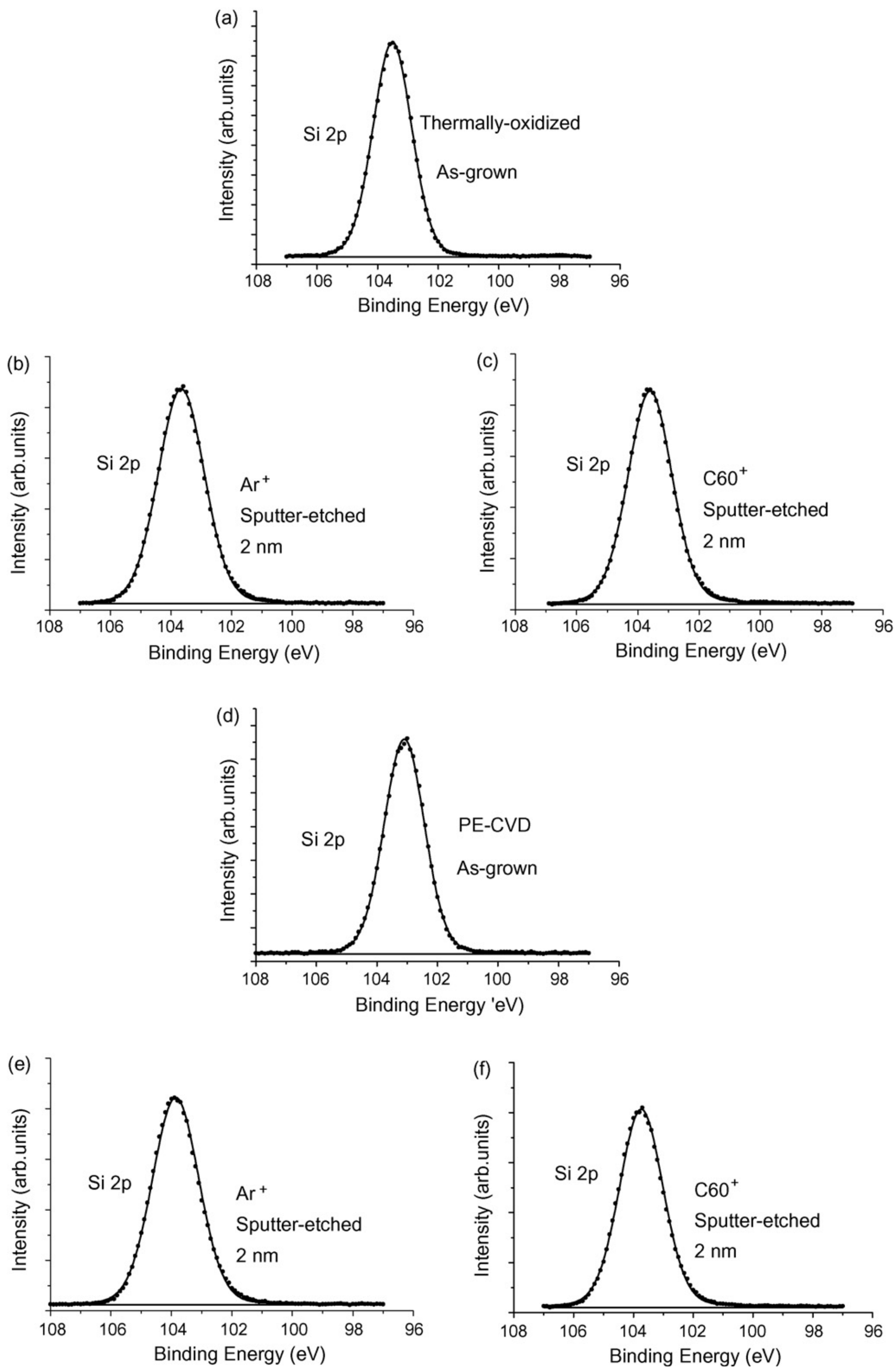

Fig. 1. XPS spectra from SiO_2 films on Si: (a) as-grown surface of a thermally-oxidized film; (b) 2-nm depth from the surface for the thermally-oxidized film sputter-etched using 500 V Ar^+ ions; (c) 2-nm depth from the surface for the thermally-oxidized film sputter-etched using 10 kV C_{60}^+ ions; (d) as-grown surface of a CVD oxide film; (e) 2-nm depth from the surface for the CVD oxide film sputter-etched using 500 V Ar^+ ions; and (f) 2-nm depth from the surface for the CVD oxide film sputter-etched using 10 kV C_{60}^+ ions.