Preparation of Silica Thin Films by Reduction of Aqueous Solution

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INTRODUCTION

Silica (SiO_2 as main component) films have been vigorously used in electronics, optics and surface treatment field, especially as gate insulators, interlayer dielectrics and chip passivation for thin layer of large-scale integration (LSI) circuit, antireflective films on glasses *e.g.*, cathode ray tube, protecting films of metals from corrosion, of transparent polymer sheets (polycarbonate, polymethylmethacrylate, etc.) and of glasses. Essential preparation methods of silicon dioxide films include thermal oxidation of a silicon substrate, chemical vapor deposition (CVD), reactive sputtering and sol-gel processes. The electrolytic methods in aqueous solutions have several advantages over other techniques because it is performed at atmospheric pressure, at a temperature below 373 K, under low environmental hazard and with a simple and inexpensive apparatus. The main purpose of this work is thus laid in the preparation of silica thin films via potentiostatic electrolysis of an aqueous solution and characterization of them.

EXPERIMENTAL

Cathodic potentiostatic electrolysis (*vs.* Ag/AgCl electrode) was performed by the polarization of conductive substrates (a copper, stainless steel, platinum plate, *et al.*) in an electrolyte solution of a 0.1 mol dm^{-3} ammonium hexafluorosilicate ($(NH_4)_2SiF_6$). The content of silicon in deposits was determined with an X-ray fluorescent spectrometer. The atomic composition analysis of the film for the surface and bulk phase was performed by X-ray photoelectron spectroscopy (XPS) with Ar^+ sputtering. A Fourier transform infrared (FT-IR) spectrophotometer was used for the reflection absorption measurements.

RESULTS AND DISCUSSION

The increase of Si content in the deposits shown in Fig. 1 indicates the growth of films according to electrolysis time and decreasing potential. Postulating that the density of the film was 2.2 corresponding to that of amorphous SiO_2, the thickness of the film prepared at –1 V for 20 h was estimated to be 450 nm. Figure 2 shows the depth distribution analysis of the film. The atomic ratio of oxygen to silicon (O/Si) in the inner phase of the film within which the Cu atomic concentration is lower than 1 %, this value is 1.8-1.9 and negligible peaks of copper, fluorine and nitrogen were observed, suggesting SiO_2 as the main component of the film. IR absorption in the range 2500-3700 cm^{-1} and at *ca.* 950 cm^{-1} attributable to stretching modes of the silanol group (Si–OH) indicated the inclusion of some silicon hydroxide species in the mechanism of formation of the films. This preparation method may have practical applications in hydrophilic films on metals. Further studies on the electroless formation of films on non-conductive substrates will be exhibited.

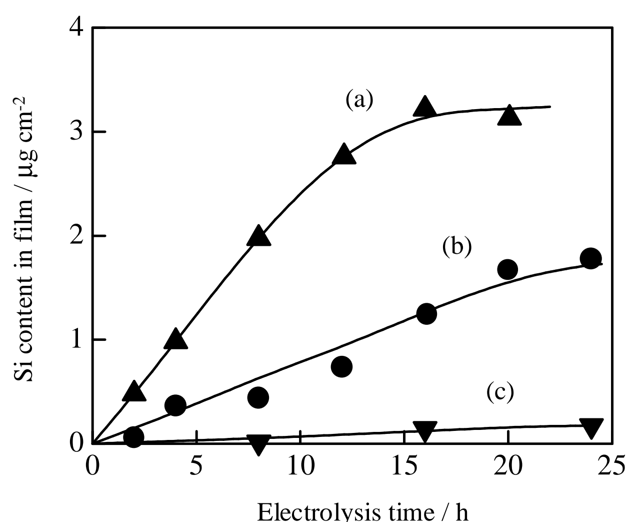

Fig. 1 Time course of silicon contents in the deposits prepared by the electrolyses at (a, closed triangles) –1.2 V, (b, closed circles) –1 V and (c, closed reverse triangles) –0.8 V.

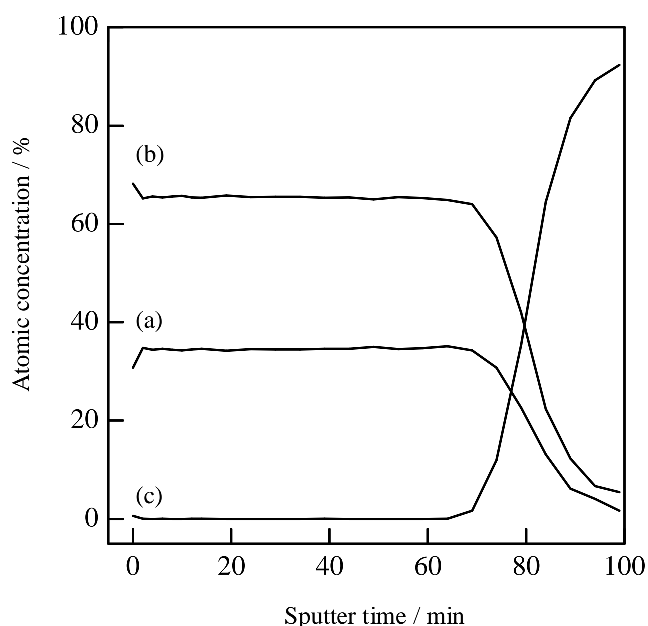

Fig. 2 XPS depth distribution atomic composition profile of (a) silicon, (b) oxygen and (c) copper of the film prepared at –1 V for 16 h on Cu substrate.