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Microhardness and structure of thick silica films prepared by vacuum deposition

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The relationships are investigated between the microhardness, density and composition of silica films 7 to 10 μm thick prepared by resistance heating and electron beam evaporation. The Vickers hardness of the film prepared by electron beam evaporation gives 180 to 620 kg mm^{-2} for varying pressures and is higher than that of film prepared by resistance heating evaporation. The silica films of higher density show higher hardness irrespective of the kinds of evaporation. The porosity of the films, which is 0 to 30% and decreases with lowering pressure, is estimated from the ratio of measured density of the film to assumed bulk density.

1. Introduction

There have been few papers on the hardness of vacuum evaporated thin films because of the difficulty of measuring their genuine hardness. Palatnik and Gladkikh [1] investigated the microhardness and microstructure of metal films (thickness: 20 to 300 μm) deposited in vacuum. Nishibori and Kinosita [2] recently studied the hardness of MgF_2 and LiF films 0.1 to 1 μm thick, using their constructed Vickers type ultra-microhardness tester. Further, hardness of TiC films made by activated reactive evaporation from 6 to 125 μm in thickness were measured by Bunshah and Raghuram [3, 4].

Evaporated silica films are used for protective films for surface mirrors and plastics, optical thin films [5, 6] insulating films for thin film devices [7]. Although optical and dielectrical properties of silica films have been widely studied, the hardness of these films in relation to their structure has not been well established. In fact, stoichiometry of evaporated silica films can be varied by film preparation conditions, e.g. pressure and deposition rate [8].

In the present work, we investigated the hardness of vacuum-deposited silica protective films. This paper describes the relationships between the microhardness, density and composition of thick silica films prepared by resistance heating or by electron beam evaporation, and these properties are examined as a function of pressure in film preparation.

2. Experimental

2.1. Sample preparation

Silicon monoxide (SiO) and fused quartz (SiO_2) were used as evaporants in the case of resistance heating (RH) and electron beam (EB) evaporation, respectively. The films were deposited on commercial glass substrates at pressures ranging from 1×10^{-3} to 5×10^{-5} torr, where the distance from the source to the substrate was 17 cm for the two evaporation methods. The rate of deposition was 1 μm min^{-1} for RH and 0.5 μm min^{-1} for EB evaporation.

The evaporated silica films over 7 μm in thickness [9] were used for measurement of hardness and density, and the films less than 2 μm thick were used for identifying their composition.

2.2. Film hardness, density and composition

The Vickers microhardness was measured, eliminating the effect of glass substrate, under a load of 25 g for a loading time of 30 sec. The hardness value was determined as the average from 10 measurements for each specimen.

The density of the evaporated silica films was determined by measuring its mass, area and thickness. The mass was measured after the specimen

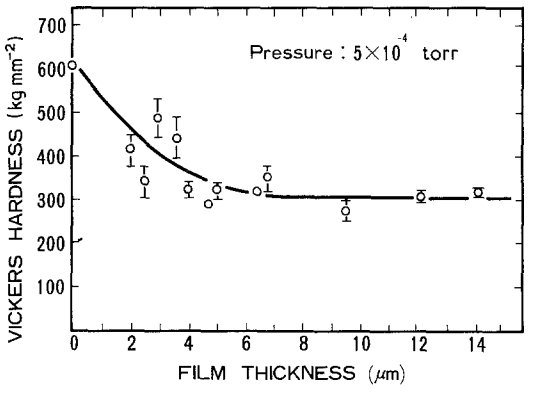

Figure 1 Vickers microhardness versus thickness of silica films evaporated on glass substrate by electron beam evaporation.

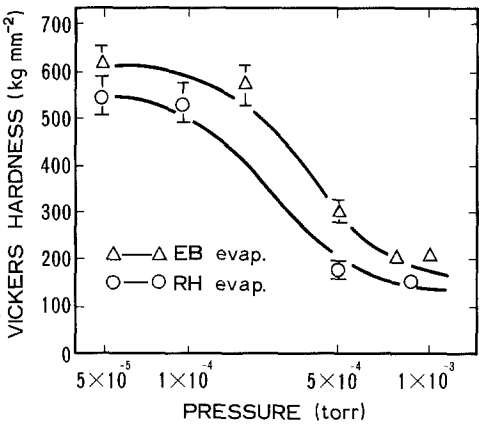

Figure 2 Variation of hardness for silica films deposited by electron beam and resistance heating evaporation as functions of pressure.

had been kept in a desiccator for 1 h after deposition to avoid water absorption into the film.

Since infrared spectroscopy is a useful method for identifying silicon oxides [8], we examined the infrared absorption spectra of the silica films deposited on KBr plates at various pressures.

3. Results

3.1. Film thickness and hardness

Preliminary experiments were made to find a minimum thickness of silica films necessary for eliminating the effect of substrate on the film hardness. The microhardness was measured for films of varying thickness prepared on the glass substrate by EB evaporation at 5×10^{-4} torr. Fig. 1 shows the results of the hardness measurements as a function of film thickness, where the open circles and bars indicate the average and scattering range of 10 measurements for each specimen. The hardness is seen to decrease with an increase of film thickness up to 6 μm, and then to stay constant at about 300 kg mm^{-2} for film thicknesses over 7 μm. Since the depth of the indenter into the film is calculated from the diamond pyramid impression to be 2.5 μm and this depth is less than the film thickness ($\sim$ 7 μm), the constant hardness value gives the geniune hardness (300 kg mm^{-2}) of the film. The higher hardness values of the films with thickness smaller than 6 μm reflects the effect of the glass substrate, the Vickers hardness of which was measured to be 610 kg mm^{-2}. Accordingly, in subsequent microhardness measurements we used the films of the order of 10 μm in thickness so that the effect of the substrate could be eliminated.

3.2. Pressure and film hardness

The variation of film hardness in relation to environmental pressure during film deposition is shown in Fig. 2 for two kinds of films, i.e. those obtained by RH and EB evaporation. The hardness of the films prepared by both evaporating methods at 1×10^{-3} to 5×10^{-5} torr was found to be 150 to 620 kg mm^{-2}. As Fig. 2 shows, the highest film hardness, 620 kg mm^{-2}, was obtainable at 5×10^{-5} torr by EB evaporation, which was almost the same hardness value as that observed for commercial glass plate (610 kg mm^{-2}) but was less than that of fused quartz (720 kg mm^{-2}).

3.3. Pressure and film density

Fig. 3 shows the relation between the film density and pressures during deposition. The density of the film made by EB evaporation at 5×10^{-5} torr was determined to be about 2.02 g cm^{-3} which

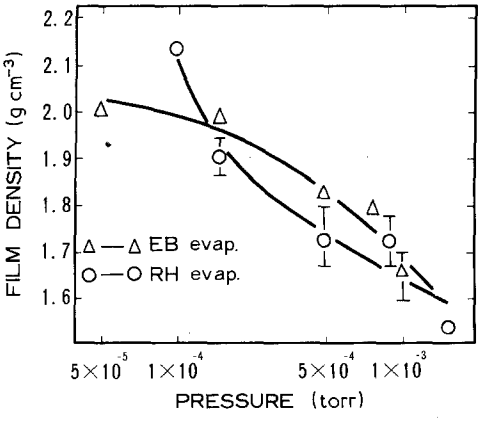

Figure 3 Film density versus pressure.

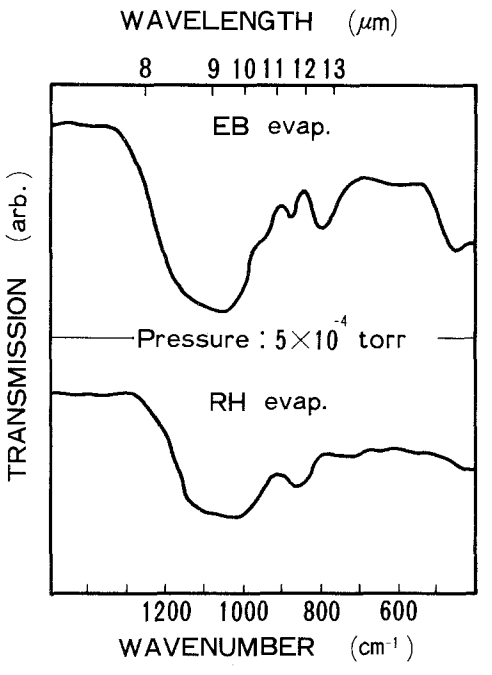

Figure 4 Infrared transmission spectra of vacuum-deposited silica films.

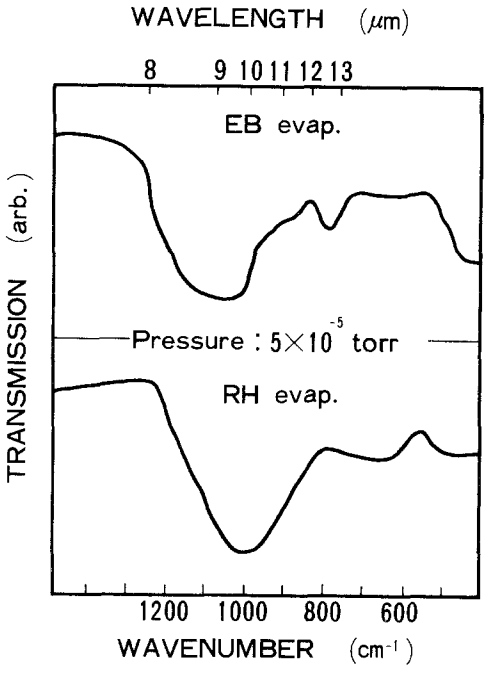

Figure 5 Infrared transmission spectra of vacuum-deposited silica films.

was less than that of fused quartz at 2.20 g cm^{-3}, while that of the films by RH evaporation at 1×10^{-4} torr was about 2.13 g cm^{-3}, which was slightly less than that of silicon monoxide (2.15 ± 0.03 g cm^{-3}) [10].

3.4. Pressure and film composition

Figs. 4 and 5 show the infrared absorption spectra of the silica films prepared by RH and EB evaporation at 5×10^{-4} and 5×10^{-5} torr. It was found that composition of the silica films differed depending upon the kinds of evaporants and evaporation methods even at the same pressure.

A moderate absorption band near 11.4 μm together with a strong absorption band at 9.6 μm, identifiable as Si_2O_3, was found for the film evaporated by RH evaporation [8]. On the other hand, the EB evaporated film showed a strong band at 9.2 μm and moderate ones at 12.5 and 11.4 μm, which means that this film consists of a mixture of SiO_2 and Si_2O_3.

In evaporating at 5×10^{-5} torr, the spectrum of the film prepared by RH evaporation showed a strong absorption band at 10 μm, identifiable as SiO. The EB evaporated film gave a strong absorption at 9.2 μm and an absorption at 12.5 μm, the same spectrum as SiO_2. As described already, the amount of oxygen combined with vaporized Si was dependent on oxygen partial pressure during deposition. The results of the analysis are summarized in Fig. 6 as relations between pressure and film composition. Furthermore, combining with the measurements of film density, the following was concluded: for the films prepared by RH evaporation, the film ranging from about 1.83 to 2.13 g cm^{-3} in density is Si_2O_3; of the films prepared by EB evaporation, the film over 2.0 g cm^{-3} in density is SiO_2 and that from about 1.65 to 2.0 g cm^{-3} is a mixture of SiO_2 and Si_2O_3.

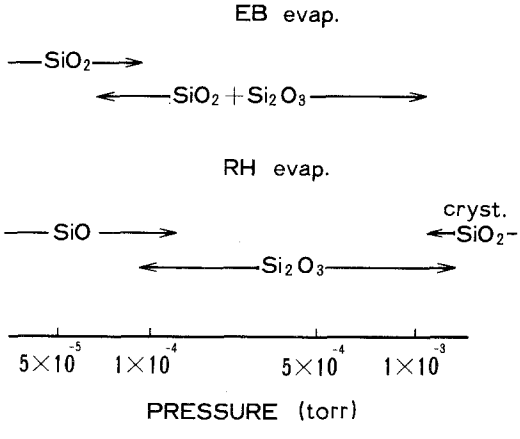

Figure 6 Composition of silica films versus pressure during evaporation.

4. Discussion

4.1. Pressure and film hardness

The highest hardness value obtained was nearly equal to that of commercial glass plate, but less than that of fused quartz (see Section 3.2). The hardness of the polished surface of a fused quartz bulk specimen, a pure amorphous SiO_2, was found to be about 750 kg mm^{-2}. As shown in Fig. 2, the highest hardness observed for the EB evaporated silica films having SiO_2 structure is 620 kg mm^{-2}, which is about four-fifths that of fused quartz. This may be ascribed to the porous character of evaporated silica films considering the result of film density in Fig. 3.

The hardness and density of the films made by RH and EB evaporation decreased gradually with increasing pressure (Figs. 2 and 3). This may be because the mean free path of vapour molecules becomes shorter with increasing pressure, and that the collision probability of vapour molecules with residual gas molecules increases. This process would produce a loose film containing many pores which can adsorb water, oxygen or nitrogen gases, and finally results in the density lowering of the film.

The hardness of silica films by EB evaporation was higher than that of the films by RH evaporation and this hardness difference was larger for lower pressures. To discuss this, we consider first that the difference of composition of the silica film depends upon the evaporation methods; the film by EB evaporation at $\sim 10 \times 10^{-5}$ torr was SiO_2 and that by RH evaporation was SiO. Also the EB-deposited film consisted of a mixture of SiO_2 and Si_2O_3 and the film made by RH evaporation was Si_2O_3 at 1 to 10×10^{-4} torr. Secondly, the density of the silica films by EB evaporation was relatively higher than that of the films by RH evaporation, as shown in Fig. 3. Although the density of the silica films by RH evaporation was higher than that of the films by EB evaporation under 2×10^{-4} torr in pressure (Fig. 3), it does not contradict the results in Fig. 8 that the hardness of the film by EB evaporation is higher than that by RH evaporation with the same density.

4.2. Pressure and film density

The density of the films decreased with increasing pressure as shown in Fig. 3; this suggests that the film contains many micro-pores in itself as described in Section 4.1. The film density was found to be about 1.6 g cm^{-3}, being independent of the evaporation methods at 2×10^{-3} torr, while the films by EB evaporation showed a higher density than that of the films by RH evaporation at 2 to 10×10^{-4} torr. From the analysis of the infrared absorption spectra (see Section 3.4), the EB evaporated film was identified as a mixture of SiO_2 and Si_2O_3 and the film by RH to be Si_2O_3 at 1 to 10×10^{-4} torr. As a result the former film has a slightly higher density than the latter one because it contains SiO_2. Although the RH evaporated film at 1×10^{-4} torr was identified to be of SiO composition and the film density to be nearly the same as the bulk density of SiO, it is actually supposed that the film contains pure silicon whose bulk density is 2.40 g cm^{-3} [11] and higher than that of SiO (2.15 g cm^{-3}).

The porosity of the film can be expressed as the ratio of true density of the film material to the measured film density. Accordingly, assuming the true density, we estimate the porosity of the films using the data in Fig. 3, as a function of environmental pressure during film deposition. Pliskin *et al.* [8], described Si_2O_3 as an intermediate oxide between SiO and SiO_2, but Namba *et al.* [12] reported that SiO film consisted a mixture of Si and SiO_2. For SiO_x film prepared by us we can not determine an accurate value of x for the film from only the infrared absorption spectra of the film, so that more detailed study is needed to examine stoichiometry of the films. We assume here the density of Si_2O_3 to be 2.175 g cm^{-3}, which is an average of bulk density of SiO (2.15 g cm^{-3}) and SiO_2 (2.20 g cm^{-3}). In the same manner the density of the mixture of SiO_2 and Si_2O_3 in ratio 1 : 1 is assumed to be 2.188 g cm^{-3}. For the Si_2O_3 film, even if the density ratio of SiO_2 to SiO varies from 1 : 0 to 0 : 1, that density $\rho_{Si_2O_3}$ lies between 2.15 g cm^{-3} (ρ_{SiO}) and 2.20 g cm^{-3} (ρ_{SiO_2}). That is, the difference ($\rho_{SiO_2} - \rho_{SiO}$) is at the most 0.05 g cm^{-3}, causing an error 0.05 g cm^{-3}/2.175 g cm^{-3} = 0.023 in the assumed value $\rho_{Si_2O_3} = 2.175$ g cm^{-3}. As this means a relative error of ± 1.2% in the calculated porosity, we consider the assumption of the ratio SiO to Si_2O_3 1 : 1 to be moderate. For the mixed film of SiO_2 and Si_2O_3, we assumed the density to be 2.188 g cm^{-3} ($(\rho_{SiO_2} + \rho_{Si_2O_3})/2$). In this case, the difference ($\rho_{SiO_2} - \rho_{SiO}$) is 0.0125 g cm^{-3}, which at most leads to a relative error of ± 0.3% in the porosity. Thus, we could calculate the bulk density of each film referring to the relation between pressure and film composition in Fig. 6 for

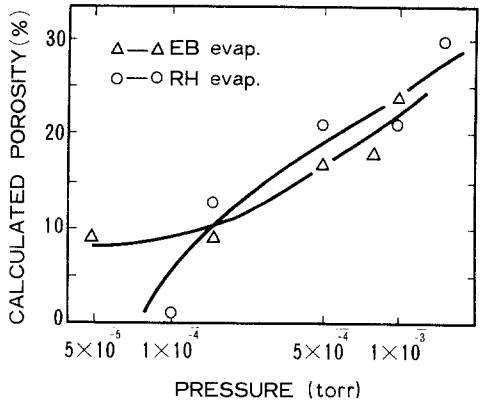

Figure 7 Calculated porosity of silica films versus pressure during film deposition.

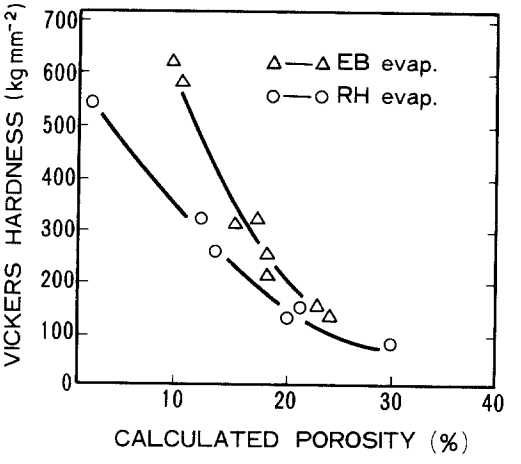

Figure 9 Vickers hardness versus calculated porosity.

both evaporation methods. The porosity of the film, i.e. the measured density of the film divided by density corresponding to the film composition, at any pressure could be deduced as shown in Fig. 7. Obviously the porosity rises with increasing pressure. In fact, we obtained a dense silica film having the porosity of nearly zero at 1×10^{-4} torr in RH evaporation and also a porous film with the porosity of about 10% in EB evaporation at a lower pressure of 5×10^{-5} torr. The porosity of the film by EB evaporation was more or less lower than that of the film by RH evaporation under 2×10^{-4} torr.

4.3. Film density and hardness

The relation between the hardness and density of the silica film is shown in Fig. 8, by rearranging the experimental results. The silica films of higher density had higher hardness irrespective of the evaporation methods. This result was considered to indicate the structure difference of two kinds of silica film, i.e. from the mixture of SiO_2 and Si_2O_3 to SiO_2 for EB evaporation, and from Si_2O_3 to SiO for RH evaporation, and further, the porosity decreases with increasing film density. Though the difference was negligibly small for the films of lower density, the hardness of the silica films obtained by EB evaporation was higher than that of the films by RH evaporation when the density was over $1.75\,g\,cm^{-3}$. This may be due to Si_2O_3 film containing many pores by RH evaporation at higher pressures as shown in Fig. 7, resulting in lower hardness at the same evaporation conditions. Infrared spectroscopy made it clear that the silica film by EB evaporation was composed of a mixture of SiO_2 and Si_2O_3. Following the procedure of estimating the porosity described in Section. 4.2, the porosity versus hardness of the silica films is given in Fig. 9. The film hardness decreases with increasing the porosity, and the film having the same porosity has a higher hardness in EB evaporation than in RH evaporation. These results suggest that fine structure of the pores in the film differs depending upon the means of preparing the film; however, on the other hand, considering that the process of film growth may not differ in each method of film preparation, it is a reasonable interpretation that the films have different compositions even when they have the same porosity.

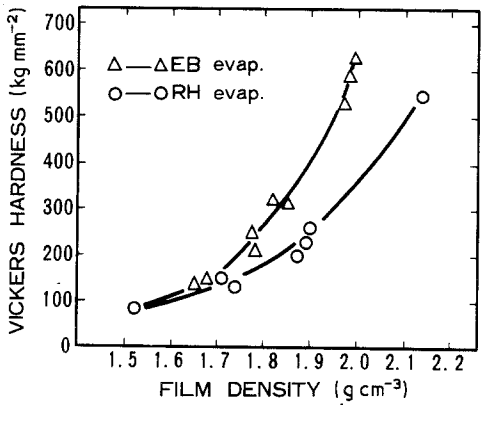

Figure 8 Relation between the density and the hardness of silica film prepared by resistance heating and electron beam evaporation at different pressures.

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