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Electron cyclotron resonance assisted deposition of protective SiO_2 films

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Electron cyclotron resonance (ECR) assisted e-gun deposition of SiO_2 films under conditions of oil-free vacuum has been studied. The SiO_2 films were deposited under different Ar^+-assisted conditions on the substrates of glass, Al and polycarbonate (PC). The optical characteristics of the layers were investigated in the VIS and IR ranges, together with their environmental stability and adhesion to substrates. The results obtained show that the films were transparent and defect-free. It was found that increases in the ion to atom ratio c_{ion} and Ar ion energy (up to 450 eV) led to film densification and, for films deposited at high deposition rate R, to the improvement of their environmental stability and adhesion to substrates.

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1. Introduction

The deposition of protective or antireflective layers based on mineral oxides on temperature–sensitive materials is a serious technological problem for the optical and micro-electronics industries. Usually, a high substrate temperature is required for depositing layers with excellent optical and micro-mechanical characteristics and good adhesion to the substrates.

Silicon dioxide is a material which is extensively used in optical thin films as a protective and antireflective coating, due to its low refractive index and ease of deposition. It is well known that the physical and chemical properties of films produced by physical vapour deposition deviate from those of the bulk materials, and depend strongly on their microstructure [1]. Ion bombardment of the films during their deposition is a technique for improving the film properties including the morphology, stoichiometry, impurity content, stress, adhesion, packing density, environmental stability, etc [2-4]. As a rule, ion bombardment of the growing film results in a more compact film microstructure, without voids and cavities [3-5]. A particular advantage is the deposition of durable coatings without addition of thermal energy [3, 6]. This opens up a number of applications of optical coatings on temperature-sensitive substrates.

Efficient ion bombardment is accomplished by ions of inert gases, most frequently argon. Gas introduction into the evaporation chamber, however, reduces the total pressure and the inert gas is inevitably buried in the growing film, which may change its microstructure and hence some film properties. The parameters which modify the quantity of inert gas trapped are the ion energy E_{ion} and the relative density of ion bombardment c_{ion}. [7, 8]. The latter is the ratio of the ion flux density (for an ion with a given E_{ion}) to the condensing material atom flux density. The quantity c_{ion} is a criterion for the degree of ion bombardment. Experimental results show that values of c_{ion} = 0.1-0.3 are typical for maximum film densification at E_{ion} of a few hundreds of eV [3, 8].

In this paper. we report our results on the influence of the Ar ion relative density c_{ion} and the energy on the properties of e-beam evaporated SiO_2 films. The changes in the optical constants, free volume, environmental stability and adhesion of the films to the different substrates are explored.

2. Experimental

Fig. 1 shows a schematic diagram of the experimental set-up, described in detail in a previous paper [9]. High vacuum coating equipment (Varian 3119) with a cryopump was used for conventional electron beam evaporation of the SiO_2 films. The source material was synthetic quartz pellets. The rate of deposition and the thickness of the SiO_2 films were controlled by an Inficon IC 6000 crystal monitoring system.

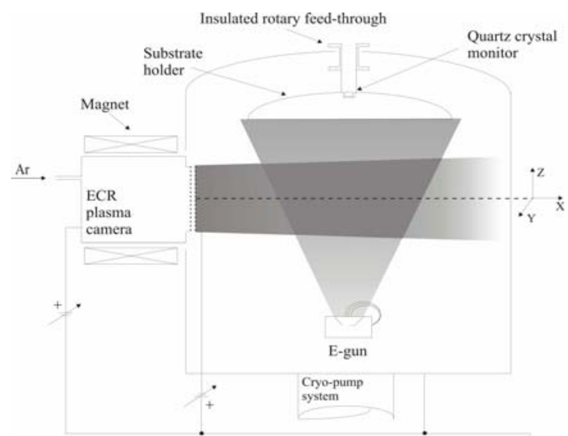

Fig. 1. A schematic diagram of the experimental set-up.

The total residual gas pressure in the system was 1×10^{-5} mbar, rising to 4×10^{-4} mbar during ion beam operation. Additional ECR plasma deposition apparatus was attached to the vacuum chamber, to provide a beam of low energy (50 – 1000 eV) Ar^+ ions incident on the substrate surface at angles within the range 40-50°. A microwave power of 350 W with a frequency of 2.45 GHz was introduced into the plasma chamber through a rectangular waveguide and a window made of synthetic quartz plate. Two graphite grids, called the screen and accelerator, were used to extract the ions. The ion flux characteristics (energy E_{ion} and current density I) depended on the total voltage U applied between the grids [9]. The ion beam current density was measured at the position of the substrates, using a Faraday cup. Due to construction limitations, the ion current at the substrate position could only be varied within a very narrow range - from 2 to 10 μA cm^{-2}. In order to change the degree of ion bombardment, SiO_2 films were deposited at two different deposition rates R of 0.1 and 6 nm s^{-1}. The relative density c_{ion} obtained is given in Table 1.

Table 1. The deposition parameters.

U_{grid} V	I μA cm^{-2}	c_{ion}	
		R=0.1 nm s^{-1}	R=6 nm s^{-1}
200	3	0.08	0.01
300	4	0.11	0.02
400	4	0.11	0.02
650	4	0.11	0.02
900	10	0.28	0.05

We chose SiO_2 single-layer coatings with thicknesses of about 150 nm for direct comparison. In each deposition, various substrates were used: silicon wafers for measuring the optical constants and film thickness, 80 nm thick Al films coated on glass plates, and optical grade polycarbonate (PC) plates for measuring the environmental stability and adhesion. All samples of PC, Si wafers and glass substrates were carefully cleaned [9].

The refractive indices n of the films were evaluated from the film reflectance, measured at normal light incidence in the spectral range λ=200-1000 nm by a Cary 5E spectrophotometer with an accuracy of 0.5%. The Wemple–DiDomenico single-oscillator model was used for describing the refractive index dispersion [10]. The free volume fraction f_b of the film was estimate by the Maxwell Garnett effective medium expression [11]:

$$\frac{(\varepsilon-\varepsilon_a)}{(\varepsilon+2\varepsilon_a)} = f_b\,\frac{(\varepsilon_b-\varepsilon_a)}{(\varepsilon_b+2\varepsilon_a)} \tag{1}$$

where ε, ε_a and ε_b are the dielectric functions of the films, bulk material (fused silica) and air respectively at λ = 700 nm. This expression is preferable when the volume fraction of the one of the phases is significantly lower than that of the other [11].

An accelerated corrosion test was applied to evaluate the environmental protection of the SiO_2 films [12]. An Al coating, 80 nm thick, with a 150 nm thick SiO_2 film on it, was immersed into a 0.2 M solution of NaOH for 2 min. The transmission T at 633 nm was then measured. The system became more transparent upon dissolution of the Al film in the case of imperfect film protection. Adhesion of films on substrates was evaluated with adhesive tape (3M Scotch Magic Type 810) according to ASTM D3359-97 [13].

3. Results and discussion

The results from XPS and XRD analyses show that stoichiometric and amorphous SiO_2 films are obtained, independently of the deposition rate.

The optical properties of films, i.e. the refractive index n and extinction coefficient k, depend strongly upon the film microstructure. Fig. 2 shows the spectral dispersion of n of 150 nm thick SiO_2 films deposited at two different rates R of 0.1 and 6 nm s^{-1} and bombarded with Ar ions with different energies. For comparison, the refractive index of bulk fused silica [14] and that of a film deposited without Ar atoms in ambient atmosphere at P = $1\text{x}10^{-5}$ mbar are also given. Vertical lines indicate the errors. As can be expected, the refractive index depended upon the deposition rate and the pressure of the residual gases. The introduction of Ar atoms into the vacuum chamber led to a significant decrease in the film refraction index. This effect was more pronounced in films deposited at lower deposition rates. The use of Ar ion irradiation during the deposition considerably influenced the refractive index of films deposited at low R (0.1 nm s^{-1}), but almost did not alter that of films deposited at high R (6 nm s^{-1}). As seen in the case of a higher ion to atom ratio (at low R) the refractive index increased with the ion energy and at E_{ion} of 450 eV reached the values for the film deposited without Ar gas at P = $1\text{x}10^{-5}$ mbar. It should be noted that further increases in E_{ion} at this value of c_{ion} were accompanied by strong sputtering of the film.

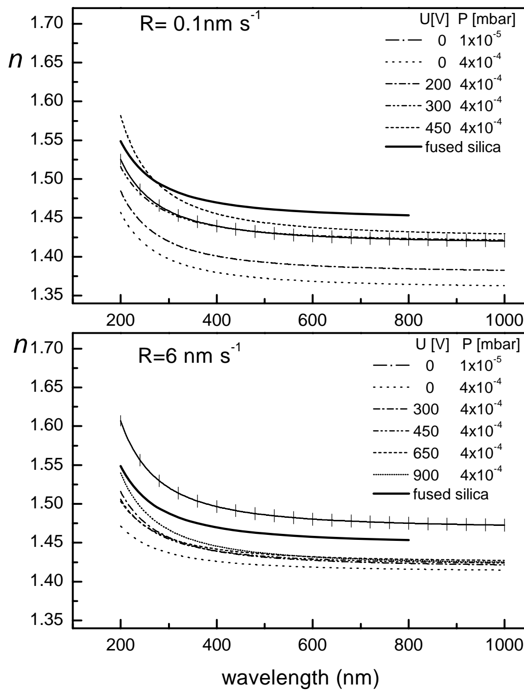

Fig. 2. Spectral dispersion of the refractive index n of 150 nm thick SiO_2 films obtained with the indicated deposition parameters.

Fig. 3 shows the free volume fraction f_b of the films, calculated on the basis of their refractive index. As seen, the free volume of films bombarded with higher ion to atom ratios decreases from 18 to 5 % with the ion energy, while bombarding with a lower c_{ion} reduces the gas volume buried in the films only by about 2 % .

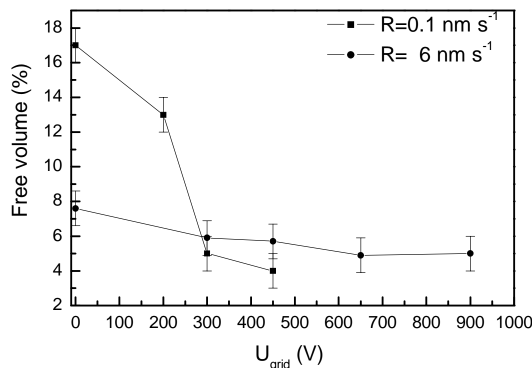

Fig. 3. Free volume in the films deposited at the indicated deposition rates, as a function of the grid voltage U_{grid}.

The results from the accelerated environmental test are shown in Fig. 4. It should be noted that immersion of an unprotected Al film in 0.2 M NaOH led to its complete dissolution in 1-2 min. In the case of an Al coating protected with silicon dioxide, the solution can get to the Al only through gaps formed at some points. The optical microscopy study shows that the increase in T obtained is due to the individual pinholes etched into the Al coating at defect sites in the protective SiO_2 film.

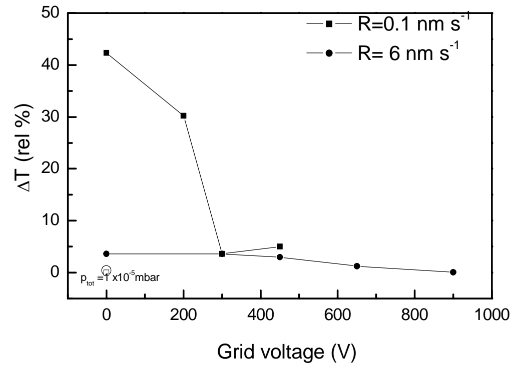

Fig. 4. Transmission of 150 nm thick SiO_2 films deposited on Al coated glass plates after immersion in 0.2 M NaOH for 2 min, vs grid voltage. $T_{untreated\ sample} = 0$; The T of treated samples, obtained at $P = 1 \times 10^{-5}$ mbar, is indicated by open square and circle.

From Fig. 4, it is seen that the densification of the films obtained at higher ion to atom ratios (at low R), with increased ion energy, also led to more corrosion resistant films. A similar tendency was observed for films ion bombarded at a low c_{ion}. Nevertheless, as a whole, films obtained at higher pressure ($P=4\times10^{-4}$ mbar), even when ion bombarded during deposition, exhibited worse environmental stabilities than those obtained at a lower P of 1×10^{-5} mbar.

The results from the adhesion test are given in Table 2. They indicate that films deposited in the presence of Ar gas in the vacuum chamber exhibited worse adhesion than those deposited without Ar. This effect was more pronounced for films obtained at a low R of 0.1 nm s^{-1}. It is seen that ion bombardment during deposition has little influence on the adhesion of the films to Al or PC substrates. A tendency for an improvement of the film adhesion with ion energy was observed only for films deposited at a high rate of 6 nm s^{-1}.

Table 2. Adhesion of SiO_2 films on Al coated glasses and PC plates, as a function of the grid voltage.

Grid voltage [V]	Adhesion			
	R=0.1 nm s^{-1}		R=6 nm s^{-1}	
	Al	PC	Al	PC
0	0A*	1A	2A*	4A*
200	1A	1A	-	-
300	1A	2A	2A	4A
450	1A	2A	5A	5A
650	-	-	5A	5A
900	-	-	5A	5A

* Same adhesion of films, obtained at $P_{tot} = 1\times10^{-5}$ mbar.

The adhesion scale according to ASTM D3359-97:

5A – no peeling or removal occurred in the area of X mark, cutted in the film. 4A – traces of peeling or removal along incisions; 3A – jagged removal along incisions occurred up to 1.6 mm; 2A – jagged removal along incisions occurred up to 3.2 mm; 1A – most of the area of the X mark under the tape was removed; 0A - removal of the film beyond the area of X mark occurred.

4. Conclusions

The results obtained show that an increase in the ion to atom ratio c_{ion} and Ar ion energy (up to 450 eV) leads to the film densification and, for films deposited at high R, to the improvement of their environmental stability and adhesion to Al and polycarbonate substrates. On the basis of the results obtained, a considerable improvement in the film properties can be expected at deposition conditions of high rates and Ar ion bombardment with an energy up to 300 eV and c_{ion} of 0.1-0.2.

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