Silicon Carbide Films as Protective and Optical Coatings

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Abstract: - The paper presents the results of experimental studies of amorphous silicon carbide films as a material for applying protective coatings, as well as for creating a submicron structure on the surface of optical elements by the method of cutting the film with laser radiation. The technology for obtaining amorphous SiC films is described. The degradation time of the film cutting of the TbFe film with the cutting protective coatings was measured and it was shown that amorphous SiC films provide more effective protection of TbFe films from oxidation compared to SiO_2 films.

Key-Words: - amorphous silicon carbide films, protective coatings, laser technology for forming a submicron structure in films

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1. Introduction

Silicon carbide films are considered mainly as a promising material for use in solar cells and in the development of new microelectronic elements based on silicon. The best results in such developments are obtained when using single-crystal SiC films, which complicates the technology of their manufacture. However, the high technical characteristics of SiC, such as high mechanical strength, hardness, thermal and chemical stability, good thermal conductivity at high values of electrical resistance, as well as a large value of the refractive index and transparency in a wide spectral region allow us to consider silicon carbide films as a good material for protective and optical coatings. An important fact is that SiC films sublimate at high temperatures, bypassing the melt stage, which allows them to be used for the manufacture of flat optical elements with a given submicron structure using powerful laser radiation.

This paper presents the results of experimental studies of amorphous silicon carbide films as a material for applying protective coatings, as well as for creating submicron.

2. Research methods

Silicon carbide films are obtained by molecular beam and gas transport epitaxy methods, by cathodic and ion sputtering methods, as well as by various electrochemical deposition methods. In our work, SiC films were produced by magnetron or ion beam sputtering on glass substrates or on fused quartz substrates. A feature of our technology is that as sputtering targets we used highly dispersed (*d=20–30 microns*) silicon carbide powder, in which each SiC crystallite was enriched with silicon. Enrichment with silicon (about *5%*) was carried out at the stage of obtaining the silicon carbide compound. The technology we used allowed us to obtain amorphous films with high strength and hardness indicators with good adhesion of the film to the substrate. The amorphous structure of the films is confirmed by electron diffraction.

In the work SiC films with a thickness of *20 nm* to *120 nm* were studied. Measurements of the optical characteristics of the films showed that our films have high transparency in the wavelength range $\lambda = 0{,}5 - 1\ \mu m$ and their refractive index $n>2.5$.

When determining the characteristics of SiC films as a protective coating, we used the accelerated aging method [1]. This method is based on the statement that any degradation process depends on temperature and is described by a certain activation potential. To assess the effectiveness of SiC films as a protective coating, we measured the degradation times of amorphous ferrimagnetic films with perpendicular anisotropy TbFe when using a protective coating of different materials. The choice of TbFe films is based not only on the fact that these films are well studied as a material for magneto-optical information recording [2, 3], but also on the fact that terbium atoms interact extremely strongly with oxygen atoms, which causes strong oxidation of TbFe films in air. It is known [2, 3] that a change in the relative concentration of interacting Tb and Fe atoms in amorphous ferrimagnetic TbFe films causes a significant change in the coercive force of the film H_c (from $Hc>10^6$ *A/m* for the composition at the compensation point $Tb_{22}Fe_{78}$ to $H_c \approx 5x10^4$ *A/m* for the composition $Tb_{17}Fe_{83}$). It should also be noted that the value of H_c can be easily and accurately controlled using magneto-optical measurement methods.

We measured the change in the coercive force H_c of the TbFe film after several hours of annealing at different temperatures T (from $T= 40^0$ C to $T= 160^0$ C) and, based on the measurement results, determined the degradation time τ_H of TbFe films at room temperature based on the following expressions

$$H(t,T) = H(T)e^{-\frac{t}{\tau_H}}$$
$$H(T) = H_0 e^{-\left(\frac{kT}{W_H}\right)^l} ; \qquad (1)$$

where H_0 is the coercive force of the film at temperature $T=0$ K, W_H is the activation potential of the degradation process, k is the Boltzmann constant, τ_H is the degradation time at temperature T, t is time, l is a numerical coefficient close to unity.

When developing a laser technology for forming a submicron structure on the surface of large-area optical parts, two tasks need to be solved. The first of them is related to the development of a technological process for forming such a submicron structure under the action of laser radiation, and the second is related to the development of a system for moving a laser beam with nanoscale accuracy. We studied the process of forming a submicron phase structure in amorphous SiC films using a special stand, the scheme of which is presented in Fig. 1.

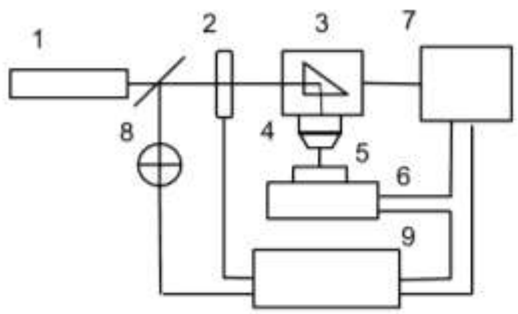

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Fig. 1. Scheme of the stand for forming submicron structures in films by laser radiation: 1 – argon laser, 2 – acousto-optic modulator, electro-optic modulator, 3 – linear displacement motor along the x coordinate, 4 – micromotor with a microlens, 5 – substrate with film, 6 – linear displacement motor along the y coordinate, 7 – laser displacement meter, 8 – photodetector, 9 – computer control unit.

The submicron structure is created by the radiation of a continuous single-mode argon laser 1 with a power of *6 W*, which is modulated by high-frequency acousto-optic modulators 2 at a frequency of *230 MHz* and focused on the substrate with a film by a microlens using an autofocus micromotor 4. Continuous or stepwise movement of the laser beam focusing point on the film surface is carried out by two linear motors 5 and 6, which are installed on high-precision aerostatic guides. The laser displacement meter 7 allows you to control the position of the laser beam focusing point on the substrate in x and y coordinates with an accuracy of up to *100 nm*. The stand is controlled by a personal computer 9. All optical-mechanical units of the stand are installed on a vibration-insulated table.

Our stand provided focusing of the laser beam on the film surface $d< 0.5$ μm with a radiation modulation depth of at least *20 dBel*. The focus point was moved continuously or discretely to a given step with an accuracy of no worse than 0.1 μm. Instead of the linear displacement motor along the y coordinate, it was possible to use an aerostatic spindle for rotating the substrate with the film at a constant angular velocity from *2* to *30* revolutions per second with an angular velocity instability of no worse than 10^{-5}. Such a replacement allowed forming a circular submicron structure on the substrate.

3. Results and Discussion

When studying the characteristics of amorphous films SiC as a protective coating, we compared these films with SiO_2 and SiO films. Our measurements showed that $Tb_{21}Fe_{79}$ films without a protective coating oxidize very quickly when they are transferred from a vacuum chamber to air. Within ten minutes, not only the coercive force of the film changes significantly, but also the magneto-optical readout signal drops to zero. In Tb21Fe79 films with a protective coating with a thickness of h=50-100 nm, the coercive force almost does not change at room temperature for several tens of hours. Fig. 2 presents the results of changes in the coercive force of two-layer films $SiC/Tb_{21}Fe_{79}$, $SiO_2/Tb_{21}Fe_{79}$ and $SiO/Tb_{21}Fe_{79}$ with a protective coating with a thickness of $h=60$ nm on a fused quartz substrate during their prolonged heating at different temperatures. The measurement results show that amorphous SiC films provide more effective protection of TbFe films from oxidation compared to SiO2 films. SiO films weakly protect TbFe films from oxidation, which may be due to the migration of oxygen atoms through this film. Processing the results of the time and temperature dependences of the coercive force of the $SiC/Tb_{21}Fe_{79}$ film shows that the protective coating with an amorphous SiC film significantly increases the degradation time of the $Tb_{21}Fe_{79}$ film. At $T=20^0$ *C*, the value of τ_H becomes greater than *2* years, which confirms the high technical performance of the protective coating based on the amorphous silicon carbide film.

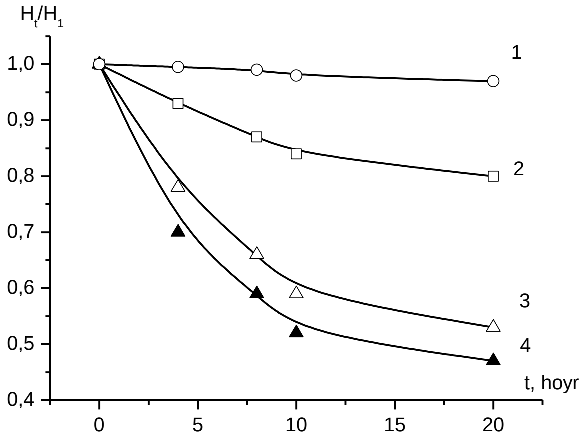

Fig. 2. Change in coercive force of $Tb_{21}Fe_{79}$ films after heating at different temperatures: 1 – $SiC/Tb_{21}Fe_{79}$ film, $T=80^0$ *C*; 2 – $SiC/Tb_{21}Fe_{79}$ film, $T=160^0$ *C*; 3 – $SiO_2/Tb_{21}Fe_{79}$ film, $T=160^0$ *C*; 4 – $SiO/Tb_{21}Fe_{79}$ film, $T=80^0$ *C*.

Studies of the process of forming a submicron structure in amorphous SiC films by powerful laser radiation showed that the above-described setup scheme allows you to obtain a regular submicron structure on the surface of large-area optical parts. The results of the obtained submicron structure will also depend on the thickness and thermophysical parameters of the film and substrate material and on the intensity and duration of the laser pulse [4]. Moreover, these dependencies can be nonlinear, which is due to the dependence of the absorption capacity and thermophysical characteristics of the amorphous SiC film on temperature. It is quite difficult to take into account the influence of all these factors, however, the experimental selection of the film cutting modes by laser radiation with a nonlinear dependence of absorption allows us to obtain the value of the minimum size of the formed structure r_0 is several times smaller than the diameter of the focused laser beam. The minimum size is the size of the focused laser beam d0 and is given by the microlens aperture *NA=0,62* and the light wavelength λ*=488 nm*, which gives $d_0 < 500$ *nm*.

A necessary condition for the formation of a submicron structure in a SiC film is that the intensity of the laser beam radiation I_0 in the center must give a film heating temperature in the center of the beam $T(r_0)$ greater than the film sublimation temperature T_s. To estimate the minimum intensity I_0, the following formula can be used [5]

$$T\left(r_0\right)=T_s\exp\left(-\frac{r_0^{\ 2}}{d_0^{\ 2}}\right)\left[\frac{\left(\pi\sigma\right)^{1/2}}{\beta}S\tau_i^{\ 1/2}-\frac{\pi\sigma S}{2\beta^2}\ln\left(1+\frac{2\beta\tau_i^{\ 1/2}}{(\pi\beta)^{1/2}}\right)\right], (2)$$

where $S=\varepsilon hI_0/\chi_1T_s$, τ_i is the laser pulse duration, σ and β are the ratio of thermal diffusivity to thermal conductivity for the film material and optical substrate, ε, h and χ are the dielectric constant, thickness and thermal conductivity coefficient of the film. In the continuous mode of movement of the laser beam focusing point, the duration of the laser pulse can be replaced by the time of passage of the focusing point of the transverse size of the focused beam d_0.

The results of experimental studies have shown that the width of the evaporation line of the SiC film depends on its thickness. With a film thickness of h_0*=20 nm*. a line with a width of d_0*=0.1* μm can be obtained (Fig. 3).

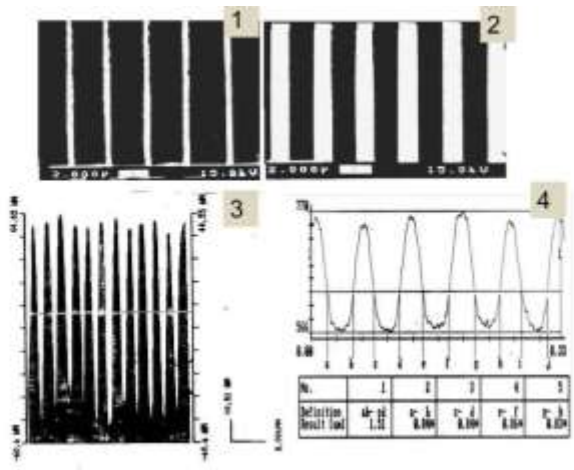

Fig. 3. Photographs, profilogram and phase contrast pattern in tracks formed in amorphous SiC films of different thicknesses by an argon laser: 1 – *h=20 nm*, 2 – *h=60 nm*, 3 – *h=100 nm*, 4 – *h=40 nm.*

In thinner films, the line width during laser cutting can be even smaller, but the phase contrast of the picture decreases. In thicker films, the depth of the cut in the film increases, which leads to an increase in phase contrast, but at the same time the transverse size of the cut line increases. With an increase in the intensity of laser radiation, the width of the cutting line increases and the destruction of the optical substrate may occur. The phase contrast pattern of the marked glass optical substrate in Fig. 3, measured on a special microscope from the air side. It is clear that when measuring from the side of the optical substrate, the phase contrast would increase by two and a half times due to the large value of the refractive index of the silicon carbide film.

4. Conclusion

Our studies have shown that the vacuum sputtering method of specially manufactured silicon carbide targets enriched with silicon allows us to obtain high-quality amorphous silicon carbide films. Such films not only have high mechanical, thermal and chemical stability and good thermal conductivity, but are also transparent in a wide range of the visible spectrum and have a large refractive index. In addition, SiC films sublimate at high temperatures, bypassing the melt stage, which makes them a promising material in laser surface treatment technology. All this allows us to state that amorphous carbide films are a good material for protective and optical coatings, on the basis of which it is possible to manufacture optical elements with a submicron structure on the surface. It should be noted that this technology for forming a submicron structure allows for direct control during the manufacturing process.

The results of our studies of the protective characteristics of amorphous SiC films showed that they provide more effective protection of TbFe films from oxidation compared to SiO2 films. Using a special stand that provided submicron precision movement of a sharply focused laser beam along two coordinates, a regular submicron structure with a minimum size of an individual element of several hundred nanometers was formed in amorphous SiC films.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

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Conflict of Interest

The author has no conflict of interest to declare that is relevant to the content of this article.