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Optical properties, form of granules and electronic parameters of binary Al/Cr composites

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Abstract. Optical and structural properties of ultrathin binary Al/Cr composites were investigated in this paper. We ascertained that the samples did not have a long-range order, and their optical properties are defined by resonance of optical conductivity in granules as a result of collective electron oscillations induced by external light wave. The granules have spherical or ellipsoidal shape depending on value of substrate surface roughness. We have also established that the value of substrate roughness does not have an influence on granule sizes and is defined only by its shape. Studying electronic properties of Al and Cr (plasma frequency, concentration of charge carriers, effective free path of electrons, radii of granules) gave an opportunity to determine the features of conductivity in Al and Cr granules.

Keywords: binary composite, granule, absorption peak, roughness, electronic parameters.

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1. Introduction

Discovery of giant magnetoresistance in composites formed by nonmagnetic high-conductive metal with embedded ferromagnetic or antiferomagnetic granules [1] at the beginning of 90th gave an impulse to begin investigations of their properties. These samples are used broadly as registering media in optical recording due to isotropy of their magnetooptical properties concerning direction of external magnetic field. Besides, these materials are used in electrorelay. Making a new multilayer composites with optimal parameters calls for profound studying their electronic structure and clear idea of changes in internal structure and in some physical properties of such films.

The purpose of this paper is to determine the electronic parameters of Al and Cr, namely: concentration of charge carriers, size of granules, effective free path of electrons, etc., on the basis of investigations of optical properties and structural characteristics of ultrathin binary Al/Cr composites.

2. Experiment

Binary composites (in all 9 samples) were sputtered by thermal evaporation at the pressure about 10^{-7} Torr on glass substrates heated to the temperature 150°C. Thin Al and Cr layers were successively sputtered on the substrate. Then thick layer of SiO_2 (100-110 nm) was applied. In that way the possibility of film oxidation in the open air was prevented. The samples conserved their optical properties over several months. To study the influence of substrate surface parameters on film properties normal deviation of substrate profile line from plane R_A:

$$R_A = \frac{1}{N}\sum_{i=1}^{N}|h_i| \tag{1}$$

was determined using Taylor-Hobson profilometer before sputtering (h_i is a size of peak or crevice with number i, N is a number of peaks and crevices).

Determination of optical parameters for our samples was realized by means of spectroellipsometrical investigations according to the Beatty method. We found the indexes of refraction, absorption and thickness of films by solving the inverse problem of ellipsometry. Then we determined real and imaginary parts of complex dielectric permeability. We determined the value of filling factor q (part of metal in the volume of the film) and form of the metal granules using the Hampe [2] and Grechko [3] theories for granular films. The main parameters for our samples are represented in Table 1.

Table 1. The main parameters of binary Al/Cr films: thickness of Al and Cr layers, value of substrate roughness and filling factors.

№	Sample	Film thickness		Normal deviation of substrate profile line from plane, R_A, mm	Filling factor for Al / Cr layers	Size of grain for grinding of substrate, D_g, mm
		d_{Al},nm	d_{Cr},nm			
1	Al/Cr	1.65	1.32	< 0.01	0.23 / 0.20	—
2	Al/Cr	1.85	1.35	< 0.01	0.12 / 0.10	—
3	Al/Cr	1.57	1.54	< 0.01	0.15 / 0.04	15
4	Al/Cr	1.57	1.60	< 0.01	0.10 / 0.08	20
5	Al/Cr	1.68	1.76	0.040	0.51 / 0.42	8
6	Al/Cr	2.02	1.91	0.181	0.49 / 0.35	2
7	Al/Cr	2.10	2.15	0.680	0.57 / 0.49	4
8	Al/Cr	2.62	2.15	< 0.01	0.35 / 0.21	10
9	Al/Cr	2.37	2.35	1.3	0.50 / 0.40	6

3. Results and discussion

Figs 1 and 2 show the spectral dependencies of optical conductivity $\sigma = \omega\varepsilon_2/4\pi$ on wavelength of incident light for Al and Cr layer in samples 5 - 7 and 9 (other samples display conformable type of curves). Analysis of such dependencies permitted to draw following conclusions. As the curves $\sigma(\lambda)$ have no absorption peaks concerned with interband transitions (at the wavelength $\lambda \sim 800$ nm for Al and at $\lambda \sim 600$ nm for Cr), which are specific to bulk metals, all the samples are amorphous films that have no clear crystalline structure with long-range order.

At the same time there are absorption peaks at the region of 430 - 450 nm for Al layers in the samples 7 and 9 (curves 1, 2 in Fig. 1) and for Cr layers in the samples 5 - 7 and 9 (curves 1-4 in Fig. 2). Only for this peak we have the decrease of the s value at the reducing of λ. The large absorption peak is in ultraviolet with $\lambda < 300$ nm for all the samples. The absorption maxima at the $\lambda \sim 440$ nm are wide and diffuse enough. In concordance with [4], such peaks exist in granular films when granules do not form the certain ordered structure. This fact is the evidence of lack of clear far order in granule arrangement in the film.

Thus, there are two absorption peaks both in Al layer and Cr layers for two binary composites (samples 7 and 9) – one at the $\lambda \sim 440$ nm, another at the $\lambda < 300$ nm. On the other hand, there are two absorption peaks in Cr layers only (at the same wavelength) for the samples 1, 2, 5, 6. The Al layers in these samples reveal only one peak at the wavelength $\lambda < 300$ nm. The peak at the $\lambda < 300$ nm is produced by plasma oscillations of charge carriers in spherical Al and Cr granules in thin films [2], the peak at the $\lambda \sim 440$ nm is stimulated by additional oscillations of charge carriers in ellipsoidal Al and Cr granules [3].

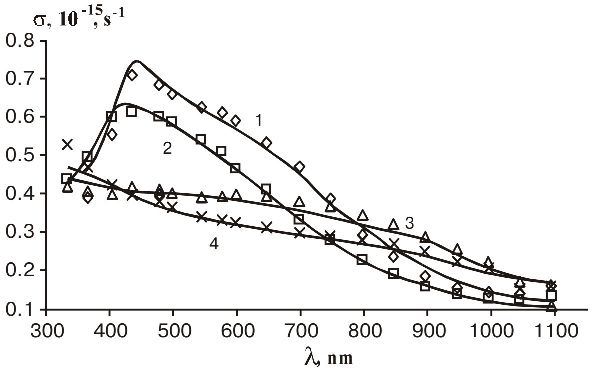

Fig. 1. Dependence of the optical conductivity, σ, on wavelength, λ, for binary Al/Cr films for Al layers (1 – sample 7, 2 – sample 9, 3 – sample 5, 4 – sample 6). —— - theoretical curve; □, Δ, ×, ◇ – experimental data.

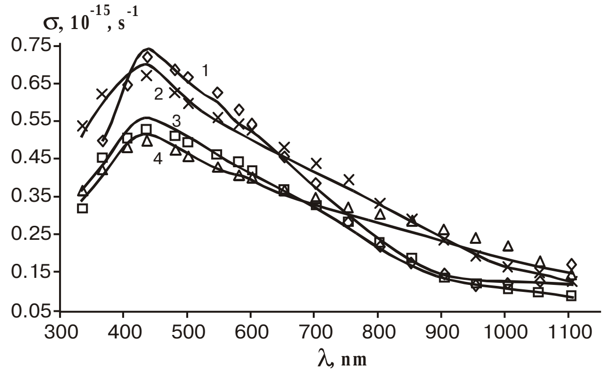

Fig. 2. Dependence of the optical conductivity, σ, on wavelength, λ, for binary Al/Cr films for Cr layers (1 – sample 7, 2 – sample 9, 3 – sample 5, 4 – sample 6). —— - theoretical curve; □, Δ, ×, ◇ - experimental data.

Using the Hampe and Grechko theories for optical properties of dispersion medium with non-contact metal spherical and ellipsoidal granules, respectively, the spectral dependencies of real and imaginary parts of complex dielectric permeability were calculated. Good agreement of theoretical and experimental curves testify to spherical form of Al and Cr granules in the samples 3, 4, 8 but in the samples 1, 2, 5, 6 only Al granules have the spherical form. In the samples 7 and 9 both the Al and Cr layers consist of ellipsoidal granules, but only Cr layers have such form of particles in the samples 1, 2, 5, 6. Some differences between the experimental and theoretical results are explained by some distortions of granule surfaces in comparison with the form of ideal spheroid or ellipsoid of rotation and with the presence of disordering in arrangement and orientation of ellipsoids. The Grechko theory provides for residence all of granules in lattice points and equality of their orientation. It is such displacement that, contrary to arrangement of granules, explains the reduction of *s* values at the peak wavelength and fuzziness as well as widening of peaks, too. At the same time, most of ellipsoidal granules are orientated equally, but we are not able to observe two distinct absorption peaks in the optical conductivity spectra.

Moreover, the theory we have used does not take into account an existence of high-field interactions between granules whereas such interaction is influential enough by increasing of filling factor [5]. It happens due to converging of metal particles that results in enlargement of the role of high-field short-range multipoles.

It is known that increasing of filling factor *q* results in displacement of absorption peak induced by collective oscillations of charge carriers in metal granules to the long-wave region [5, 6]. But in our samples such peaks are located at the identical wavelengths. Effect of substrate material on granule sizes and optical properties of Al films were studied in [7]. It turned out that modification of granule sizes gives rise to changes of intensity of the interband absorption peak but does not provoke the displacement of the peaks. Thus, we can assert that both granule shape and sizes vary by the transition from one sample to another. Fastening position of the absorption peaks to the place of experimental maxima we have determined the value of form factors for ellipsoids L_1, L_2, L_3 ($L_1 = L_2 \neq L_3$ for ellipsoids of rotation, $L_1 + L_2 + L_3 = 1$, L_i – defines an ellipsoid oblongness along i – axis). In that way we have estimated the form of the granules. The values of L_1, L_2 and L_3 for the samples with ellipsoidal granules are shown in Table 2. Comparison of these data and the values of substrate roughness allows to draw a conclusion of increase of granule oblateness when they are formed on the surfaces with bigger roughness (samples 7, 9).

Table 2. The form factors for the samples with ellipsoidal granules (L_1+L_2+L_3=1, for ellipsoids of revolution L_1= L_2).

№		L_1	L_2	L_3
7	Al	0.25	0.25	0.5
	Cr	0.26	0.26	0.48
9	Al	0.25	0.25	0.5
	Cr	0.2	0.2	0.6
1	Cr	0.28	0.28	0.44
2	Cr	0.29	0.29	0.42
5	Cr	0.3	0.3	0.4
6	Cr	0.27	0.27	0.46

Using the values of frequency ω_{0eq} when our samples have the absorption peak in the near ultraviolet calculated on basis of the Hampe and Grechko theory, we have estimated the value of plasma frequency ω_p for our films. We used the following equation:

$$\omega_p = \sqrt{\frac{3\varepsilon_m}{1-q}}\,\omega_{0\varepsilon q}\,, \tag{2}$$

where ε_m is a dielectric permeability of media with embedded granules, q is a filling factor. Using the value of ω_p we can determine the concentration of conduction electrons in granules:

$$N = \frac{m^* \omega_p^2}{4\pi e^2} \tag{3}$$

The results of ω_p and N calculations are shown in Table 3. Juxtaposing these data with the ω_p and N values for bulk Al and Cr (Al: $\omega_p = 1.49 \cdot 10^{16}$ s^{-1}, $N = 6.57 \cdot 10^{22}$ cm^{-3} [8,9], Cr: $\omega_p = 6.32 \cdot 10^{15}$ s^{-1}, $N = 1.1 \cdot 10^{22}$ cm^{-3} [8]) permits to draw next conclusions. The plasma frequency ω_p for our Al films is equal to ω_p for bulk metal, but the value of the concentration of conduction electrons N decreases approximately by 30%. It associates with the decrease of electron effective mass, m^*, in the Al granules. Quotient of conduction electrons quantity to Al atoms quantity per volume unit (number of conduction electrons per one atom) is equal to 0.7 for our samples. It is significantly less than the same quotient for bulk metal that is 1.09. Reducing effective mass m^* is related with lack of long-range order in the films and with diminution of frequency of electron collisions with Al atoms and impurities. Effective free path of electron is approximately equivalent to the granule sizes, i.e. m^* as a measure of electron inertial properties is decreased.

At the same time, the plasma frequency for the Cr films is 2.1 - 2.3 times larger than that for bulk chromium. N and m^* are larger too (by 3.5 - 3.8 and 1.65 times, respectively). Therefore, there is a quite opposite trend for Cr as compared to Al. Explanation of this fact is that *d*-electrons make more considerable contribution to conductivity mechanism of Cr granules.

Further task in investigations of Al and Cr films was the determination of the granule sizes and the estimation of effective electron free paths in granules. In this case we issued the following arguments. When the granule diameter become less than electron free path in the bulk metal, l_M, an average electron free path, l_{aver}, is determined by electron interactions with film surface, and the average electron free path is equal to radius of particles R [6]. Relaxation time is

$$\frac{1}{\tau_{\text{еф}}} = \frac{1}{\tau_\infty} + \frac{v_F}{R} \tag{4}$$

where $\tau_\infty = l_\infty / v_F$ is a relaxation time for electrons in bulk metal, v_F is a speed of electrons on Fermi level. We can note (4) in the next form:

$$\frac{1}{l_{ef}} = \frac{1}{l_\infty} + \frac{1}{R}\,. \tag{5}$$

Thus, the value of granule radius is defined by the ratio:

$$R = \frac{l_{ef} \cdot l_M}{l_M - l_{ef}}\,, \tag{6}$$

We can write down the value of the effective electron free path for our samples l_{ef} [9]:

$$l_{ef} = v_F / \gamma\,, \tag{7}$$

At the same time,

$$l_M = v_F^0 / \gamma_M\,, \tag{8}$$

$$v_F = v_F^0 \sqrt{N / N_{val}}\,, \tag{9}$$

where v_F^0 is a speed of free electrons at the concentration N_{val}, N_{val} is a concentration of valent electrons, γ_M is a relaxation frequency for bulk metal.

Using the values of g and N for our samples and the values v_F^0 (Al) = $2.02 \cdot 10^8$ cm/s [9], v_F^0 (Cr) = $2.46 \cdot 10^7$ cm/s [10], γ_M (Al) = $1.21 \cdot 10^{14}$ s^{-1} [8], γ_M (Cr) = $0.49 \cdot 10^{14}$ s^{-1} [8], N_{val}(Al) = $18.1 \cdot 10^{22}$ cm^{-3} [9], N_{val}(Cr)=$10.48 \cdot 10^{22}$ cm^{-3} [10] we have calculated the values of granule radii R, speed of free electrons on the Fermi level, v_F, and the effective free path, l_{ef}, for electrons in Al and Cr films. The results are shown in Table 3.

Table 3. The values of plasma frequency, ω_p, concentration of conduction electrons, N, speed of electrons on Fermi level, v_F, effective free path of electron, l_{ef}, and radius of granule, R, calculated on basis of experimental data.

№		Filling factor, q	Plasma frequency ω_p, 10^{16} s	Concentration of conduction electrons N, 10^{22} cm^{-3}	Speed of electrons on the Fermi level, V_F, 10^8cm/s	Effective free path of electron, l_{ef}, nm	Radius of a granule, R, nm
1	Al	0.227	1.49	4.219	0.975	0.93	0.64
	Cr	0.2	1.471	4.166	0.155	0.56	0.30
2	Al	0.118	1.49	4.219	0.975	0.93	0.64
	Cr	0.094	1.382	3.914	0.15	0.54	0.29
3	Al	0.15	1.49	4.219	0.977	0.93	0.65
	Cr	0.04	1.402	3.97	0.171	0.64	0.34
4	Al	0.104	1.49	4.219	0.988	0.93	0.64
	Cr	0.082	1.472	4.168	0.175	0.64	0.31
5	Al	0.512	1.491	4.222	0.976	0.93	0.64
	Cr	0.419	1.366	3.868	0.149	0.54	0.29
6	Al	0.488	1.49	4.219	0.975	0.93	0.64
	Cr	0.345	1.368	3.874	0.15	0.54	0.29
7	Al	0.569	1.49	4.219	0.975	0.93	0.64
	Cr	0.494	1.375	3.894	0.15	0.54	0.29
8	Al	0.349	1.49	4.219	0.981	0.93	0.65
	Cr	0.208	1.352	3.829	0.166	0.6	0.32
9	Al	0.501	1.49	4.219	0.975	0.93	0.64
	Cr	0.403	1.362	3.857	0.149	0.54	0.29

It is necessary to note that R describes some effective radius of particle for ellipsoidal granules. This radius is equal approximately to half-sum of major and minor semiaxes of ellipsoid. The sizes of granules are almost equal to each other. The value of R begins to increase only for samples 3, 4, 8. If we compare the value of substrate roughness parameter R_A and the sizes of granules we can assert that the roughness have no influence on the granule size but only on the granule form. On the other hand, samples 3 and 8 are sputtered on the substrates with big curvature which was evoked by grinding grains with large radii: 10, 15 and 20 µm, respectively. It gives rise to roll the atoms down to grooves during the sputtering and to formation "big" granules.

One may see that the effective free path of electron does not exceed the size of granules, and it is less than the granule diameter for aluminium. Therefore, dimensional effect has an essential influence on formation of optical and structural properties of thin films.

Conclusions

Optical properties of the granular binary Al/Cr composites in the region 200-1200 nm are determined by resonance of optical conduction as a result of excitation of collective electron oscillations in ensemble of metal particles. One or two absorption peaks are observed in the optical conductivity spectra in these cases. When only one peak is present, the metal granules have a spherical form, in the case of two peaks they have an ellipsoidal form. The larger value of roughness parameter R_A results in formation of more oblate ellipsoidal granules.

The comparison of Al and Cr electronic characteristics (the plasma frequency, concentration of free charge carriers) in the granules and in bulk metals allows to determine the reduction of electron effective mass m^* in the Al granules. This fact we associate with the deficiency of long-range order in granules and with the decrease of the collision frequency of electrons with Al atoms and impurities. There are the opposite trends for the Cr granules. We explain this fact on the basis of more considerable contribution of *d*-electrons to the mechanism of Cr conductivity. It is determined that the value of substrate roughness does not affect on the granule size but only on the form of the particles.

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