with nearest-neighbor interaction. The three dimensional transition in this substance is to a state with helicoidal structure. It is therefore perfectly possible that in the temperature interval in which the system is quasi-one-dimensional the ordering of the system is close to helicoidal. There are no conduction electrons in the system and the interaction of the non-nearest neighbors is probably via direct exchange, on account of the weak localization of the *d* electrons. Of course, the most convincing confirmation of the existence of the structures described above would be a direct neutron-diffraction observation of a two-velocity structure factor.

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Thermally stimulated emission of surface polaritons

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The angular dependences of the emission spectra of heated zinc selenide films were experimentally obtained in *p*-polarized light in the frequency band of the surface polaritons in the IR region of the spectrum. The dispersion curves of the surface polaritons are reconstructed from their emission spectra. The influence of a metallic substrate on the dispersion curves of the surface polaritons of a dielectric film is demonstrated theoretically. The developed theory is in good agreement with the experimental results. The possibilities of using this method to determine the optical characteristics of metal films in an insulator-metal-insulator sandwich are discussed.

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INTRODUCTION

The thermal vibrations of atoms in condensed media can give rise to alternating dipole moments at the characteristic frequencies of the medium. These alternating dipole moments emit electromagnetic waves under certain conditions. Subject to satisfaction of the energy and momentum conservation laws, these electromagnetic waves can leave the medium and be recorded as thermal radiation. The thermal vibrations of the atoms near the free surface of a crystal lattice also produce alternating dipole moment. The magnetic field produced by them, however, is "tied" to the interface and can not "break away" from it, since the wave vector of the surface polariton on the crystal–vacuum interface is always larger than the wave vector of light in vacuum.[1] The use of prisms with anomalous total internal reflection (ATIR), as is known, makes it possible to equalize the wave vector of the light in the ATIR prism with the wave vector of the surface polariton. When this condition is satisfied, the surface polariton absorbs the light wave. If some system has absorbed light, then, in accordance with Kirchoff's law, it must emit it, i.e., the picture can be reversed. Thermally stimulated emission of surface polaritons has been investigated many times (see, e.g., [2]), but the thermal emission of surface polaritons of single crystals in the regime of inverted ATIR has so far been observed apparently only in[3].

The purpose of the present study was to check on the feasibility of observing the emission of surface polaritons of dielectric film in the inverted ATIR regime, as well as to investigate the interaction of the surface polaritons of the film with a metallic substrate (in particular, to investigate the "metallic" quenching of surface polaritons[1]).

1. EXPERIMENT

The tests were made on ZnSe films sputtered on an aluminum film, obtained in turn by sputtering in vacuum on a hot substrate. The thickness of the aluminum layers prior to the annealing was ≈ 0.1 and ≈ 1 μm, while the ZnSe film, after crystallizing annealing in an argon atmosphere, was ≈ 1 μm thick. The ATIR prism was a half-cylinder of single-crystal silican, and the size of the air gap between the prism and the sample was set with the aid of a frame of lavsan polyster film 25 to 6 μm thick, depending on the emission angle. The "sam-

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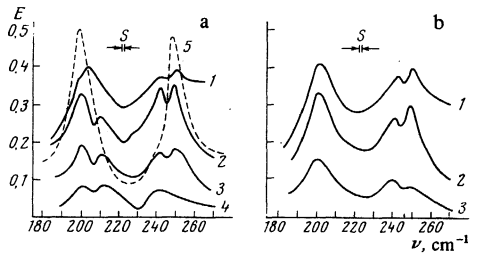

FIG. 1. (a) Emission spectra of ZnSe film 1 μm thick sputtered on an aluminum mirror ~0.1 μm thick: 1—$\theta = 16 \pm 1°$; 2—$\theta = 19 \pm 1°$; 3—$\theta = 30 \pm 1°$; 4—$\theta = 40 \pm 1°$; 5—emission of film without the ATIR prisms. b) Emission spectra of ZnSe film 1 μm thick sputtered on an aluminum film ~1 μm thick: 1—$\theta = 18 \pm 1°$; 2—$\theta = 30 \pm 1°$; 3—$\theta = 40 \pm 1°$.

ple + gap + ATIR prism" system was heated to $150 \pm 0.5°$C and replaced the radiation sources of an FIS-21 spectrometer. The emission of the "aluminum mirror + gap + prism" system, recorded under the same conditions (temperature, emission angle, frequency), was subtracted from the emission of the inverted-ATIR system. The ratio of this difference to the "black" body radiation[2,3] recorded under the same conditions yielded the relative emissivity of the system. Figure 1a shows the p-polarized spectra of the emissivity of ZnSe films 1 μm thick on an aluminum mirror ≈ 0.1 μm thick on a Pyroceram substrate, while Fig. 1b shows analogous spectra, but at aluminum-mirror film thicknesses 0.5–1.0 μm. For comparison, Fig. 1a shows (dashed) the emissivity of the same films but without the ATIR prism, at an emission angle 40°, at the same experimental geometry and at the same temperature.[3] In free thin films there should exist two surface polaritons, one polarized parallel to the film surface (with frequency $\omega_-(k_x)$), and the other polarized perpendicularly (with frequency $\omega_+(k_x)$).[4] As seen from Fig. 1a, besides the longitudinal phonon (248 cm^{-1}) and the transverse phonon (200 cm^{-1}), the emission of the film with the prism shows two surface-polariton bands, while Fig. 1b shows one ω_+ band of surface polaritons whose frequencies are practically independent of the emission angle (and hence of the wave vector k_x).

Figure 2 shows the dispersion curves, reconstructed from the experimental data, of the surface polaritons in ZnSe films sputtered on a thin aluminum mirror and on a thick one. The dispersion of the surface polariton of single-crystal ZnSe, obtained in analogy with[2], is shown for comparison (curve 3). The dispersion curves of surface polaritons of single crystals and films should differ only for small wave vectors and should coincide at large wave-vector values, when the interaction of the surface modes localized near both surfaces can be neglected. As seen from Fig. 2, the dispersion of the surface polaritons of the single crystal and of the film in contact with the metal differ not only for small wave vectors, but also at large values $k_x = \omega c^{-1} n \sin\theta$ (n is the refractive index of the prism material and θ is the emission angle). This difference between the dispersion laws of the lower surface-polariton branch in a free film and in a film on a metal is due, as will be seen from the theoretical analysis, to the interaction between the surface polaritons polarized parallel to the film surface and the conduction electrons of the thin aluminum mirror.

2. THEORY AND DISCUSSION OF RESULTS

Since the thicknesses of the ZnSe and Al films greatly exceed the lattice constant, the analysis can be carried out in the language of the macroscopic permittivity $\varepsilon(\omega)$ of the zinc selenide and of the impedance $\zeta(\omega, k_x)$ of the aluminum film. In the considered geometry, when plane interfaces are present, the electric and magnetic fields in the surface wave are of the form $\mathbf{A}(z)\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)$, where $\mathbf{k}$ is the wave vector along the interface and the z axis is perpendicular to it. If the x axis is directed along the surface-wave vector $\mathbf{k}$, then, as follows from Maxwell's equation, only the field components E_x, E_z, and H_y differ from zero ($E_y = 0$, since p-polarized light is assumed). If we stipulate for the investigated system the following boundary conditions on the two interfaces (metal–insulator and insulator–vacuum):

$$\frac{E_x}{H_y} = \xi(\omega, k_x), \qquad \frac{E_x}{H_y} = -Z_v(\omega, k_x),$$

then the equation for the dispersion law of the surface states is easily derived in the form

$$Z_d = -\frac{Z_v + \xi}{2}\operatorname{cth}\varkappa d \pm \left[\left(\frac{Z_v+\xi}{2}\right)^2 \operatorname{cth}^2 \varkappa d - \xi Z_v\right]^{1/2}, \tag{1}$$

where

$$Z_v = \frac{ic}{\omega}\left(k_x^2 - \frac{\omega^2}{c^2}\right)^{1/2},$$

$$Z_d = \frac{ic}{\omega\varepsilon(\omega)}\left(k_x^2 - \varepsilon(\omega)\frac{\omega^2}{c^2}\right)^{1/2},$$

$$\varkappa = \left(k_x^2 - \varepsilon(\omega)\frac{\omega^2}{c^2}\right)^{1/2},$$

and d is the thickness of the ZnSe film. In the considered range of frequencies and wavelengths of the surface states we have $Z_V \sim 1$, whereas for media with metallic conductivity we have $\xi \ll 1$. The second term in the radicand of (1) is therefore much smaller than the first and furthermore, since the dielectric film is thin, we have $\varkappa d \ll 1$ and hence $\coth \varkappa d > 1$. Therefore, expanding the square root in (1), we obtain

$$Z_d = -(\xi + Z_v)\operatorname{cth}\varkappa d, \tag{2a}$$

$$Z_d = -\frac{\xi Z_v}{\xi + Z_v}\operatorname{th}\varkappa d. \tag{2b}$$

Let us investigate the solution of (2a). Since $\xi \ll Z_V$,

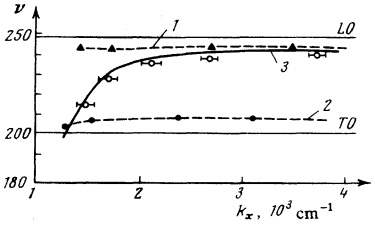

FIG. 2. Dispersion of surface polaritons in a ZnSe film on an aluminum mirror: 1—$\omega_+(k_x)$; 2—$\omega_-(k_x)$; 3—$\omega(k_x)$ for ZnSe single crystal.

it follows from (2a) that the surface-polariton frequencies $\omega_+(k_x)$ depend little on the impedance of the metal substrate. Putting $\coth \varkappa d \approx 1/\varkappa d$, we get

$$\varepsilon(\omega)=\frac{c^2k_x^2}{\omega^2}\left[1-\frac{c^2}{d\omega^2}\left(k_x^2-\frac{\omega^2}{c^2}\right)^{1/2}\right]^{-1}. \quad (3)$$

It follows from this equation that the frequency $\omega_+(k_x)$ is close to ω_{LO} when $k_x > \omega/c$ and $\Delta\omega_+(k_x)=\omega_{LO}-\omega_+(k_x)$ changes from 2.5 to 4 cm^{-1} when k_x changes from 2×10^3 to 4×10^3 cm^{-1}. Since dissipative processes come into play in a metal in the presence of $\mathrm{Re}\,\xi \neq 0$, the metal-induced quenching of the surface polariton can be obtained by taking ξ into account in (2a). The corresponding line width is obviously a quantity on the order of $\gamma \sim \Delta\omega_+(k_x) \times \mathrm{Re}\,\xi/|Z_V| \lesssim 0.1$ cm^{-1}. The experiment reveals a much larger bandwidth, which can be due to experimental errors brought about by the scatter of the registered emission angles, to the non-optimal choice of the gap between the ATIR prism and the film, as well as to the contribution of the anharmonic interactions (these increase with rising temperature. The last factor seems to cause some difference ($\lesssim 2$ cm^{-1}) between the experimentally observed $\Delta\omega_+(k_x)$ and those calculated above.

Equation (2b), in contrast to (2a), yields a solution that describes the influence of the metallic film on the dispersion law of the film's surface polariton. For an ideally conducting metallic mirror we have $\xi = 0$ and (2b) yields $Z_d = 0$, hence $\omega_-(k_x)=\omega_{TO}$. As the "metallic" properties of the substrate deteriorate, $\omega_-(k_x)-\omega_{TO}$ increases. It follows also from (2b) that the frequency of the surface state $\omega_-(k_x)$ is almost independent of k_x, since the impedance ξ depends quite weakly on k_x in the considered range of the wave vector. When the parameters of pure bulky aluminum are substituted in (2b), $\omega_-(k_x) - \omega_{TO}$ amounts to several hundredths of a cm^{-1}, so that in the experiment the surface polariton almost coincides with the transverse optical phonon, i.e., only one branch of surface polaritons should be observed (see Fig. 1b). On the other hand if the conductivity of the metallic substrate is not high, a noticeable difference between $\omega_-(k_x)$ and ω_{TO} should be observed. In the experiment with the thin aluminum-substrate film (Fig. 1a), a large deviation of the surface polariton $\omega_-(k)$ is observed. It can therefore be concluded that the impedance of the thin metallic film is not very small. It is known that the optical properties of thin aluminum films in the IR band differ greatly from the properties of the bulk metal.[5] And since we do not know of any methods of determining the impedance of a thin metallic film on a substrate on which a thin dielectric layer is sputtered, it is also impossible to estimate the value of $\omega_-(k_x)$ in this case.

From (1) we can estimate the value of ξ at which the frequency $\omega_-(k_x)$ is equal to the experimental value. This estimate yields $|\xi| \approx 0.3$. To obtain a tentative value of the conductivity of the metal account must be taken of the fact that the thickness of the metal film is small. The impedance of the metal film can be easily shown to be connected with the impedance of a semi-infinite metal by the relation

$$\xi=\xi_\infty\frac{\xi_\infty+Z_M\coth(a\delta^{-1})}{Z_M+\xi_\infty\coth(a\delta^{-1})},$$

where Z_M is the impedance of the substrate (in our case, Pyroceram), ξ_∞ is the impedance of the semi-infinite metal, and δ is the depth of the skin layer. Since the metal film is thin, $a \approx 10^3$ Å, and the skin depth of the "dirty" metal[1)] is large, we can, by putting $\coth(a\delta^{-1}) \approx \delta/a = c\xi_\infty/a\omega$, obtain the following relation (assuming $|Z_M| \sim 1$):

$$\xi_\infty^2=\frac{\omega a}{c}\frac{\xi Z_M}{Z_M-\xi}\approx\frac{\omega a}{c}\xi\sim10^{-2}\xi.$$

Consequently the permittivity $\varepsilon_M = 1/\xi_\infty^2$ of the metal film is ~300 in the infrared region at a frequency 200 cm^{-1}. The obtained value of ε_M is smaller by at least two orders of magnitude than the permittivity of a freshly sputtered metal film.

We can thus conclude from the foregoing analysis that the qualitative regularities of the theory agree well with experiment.

We note that the measured values of the deviation of the lower polariton branch $\omega_-(k_x)$ from the frequency of the transverse optical phonon can serve as a method of obtaining data on the optical properties of thin metallic films imbedded in a dielectric medium.

[1)]The aluminum mirror becomes "oxidized" in the course of the recrystallization (annealing) of the films. The mirror properties deteriorate, if for no other reason, because a constant background is observed in the emission spectra at frequencies $\omega \gg \omega_{LO}$, whereas the ZnSe film are fully transparent in this region and an ideal metal should not emit at all.

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