Influence of the conductivity of a metal substrate on the optical properties of thin insulator films

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An investigation was made of the spectral and angular dependences of the thermal radiation emitted from zinc selenide films deposited on metal (aluminum, chromium, and titanium) substrates. A strong interaction was observed between long-wavelength optical phonons in the insulator film and the conduction electrons in the metal substrate. The emissivity of metal–insulator "sandwiches" is calculated using the Kirchhoff law. The results of the calculations describe satisfactorily the experimental dependences.

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INTRODUCTION

The mutual influence of media in contact on the nature of elementary excitations is being investigated theoretically and experimentally, particularly in connection with the properties of "sandwiches" proposed as one of the structures of high-temperature superconductors. Studies have already been made of the influence of the conductivity of thin metal films on the surface polaritons in the substrate crystal[1-3] and of the interaction of surface polaritons in an insulator film with the electron subsystem of a metal substrate.[4,5] These treatments are concerned with the interaction between bulk excitations in an insulator film and the electron subsystem of a conducting (metal) film. The metal film is assumed to be between two insulators. Data on the conductivity of such films at optical frequencies are of intrinsic nontrivial interest. We shall tackle this problem by considering the thermally stimulated radiation emitted from an insulator film in the long-wavelength infrared part of the spectrum.

Thermal radiation emitted by crystals can be used to determine their optical constants (see, for example, the review in Ref. 6). The same method is applicable to the optical properties of films.[4,7,8] The emission spectra of thin films have bands whose intensities depend strongly on the film thickness d and on the angle of emission θ. An attempt is made in Ref. 7 to explain the observed radiation as the deexcitation of normal modes of crystal films (polaritons); a theory of these modes is given in Ref. 9 without allowance for the influence of the substrate. However, it is difficult to use the method suggested in Refs. 7 and 9 because polaritons in a bounded crystal are transient modes with a large radiative width and, moreover, their dispersion law consists of a multitude of branches due to the transverse quantization of electromagnetic waves in a film. One should mention here a calculation of the emissivity of films based on the Kirchhoff law and on the specific type of permittivity of an "ionic" crystal.[4] However, this calculation ignores the penetration of the film into the metal substrate. This is not justified because there is experimental evidence that the substrate conductivity has a strong influence on the optical properties of films. In view of this situation, we decided to carry out a systematic experimental and theoretical investigation of the influence of the finite conductivity of a metal substrate on the emissitivy of insulator (semiconductor) films in the long-wavelength infrared range.

1. CALCULATION OF THE OPTICAL PROPERTIES OF FILMS ON METAL SUBSTRATES

If the film thickness amounts to a few hundreds of the crystal lattice constants, the optical properties can be considered theoretically using the macroscopic permittivity $\varepsilon(\omega)$. The substrate can then be regarded as semiinfinite and its permittivity is designated by $\varepsilon_m(\omega)$. Since the transmission coefficient of such a system is zero, it follows from the Kirchhoff law that the intensity of the radiation emitted at a frequency ω along an angle θ is

$$E(\omega, \theta, T)=[1-R(\omega, \theta)]E_0(\omega, T), \qquad (1)$$

where $E_0(\omega, T)$ is the spectral intensity of the radiation emitted from a black body whose temperature is T; $R(\omega, T)$ is the reflectivity of the system for a plane wave incident at an angle θ.

The validity of the Kirchhoff law in the form given by Eq. (1) is related to neglect of the scattering of electromagnetic waves in a sandwich. This approximation is justified in the long-wavelength part of the spectrum since the intensity of the scattered radiation I_s decreases rapidly on increase of the wavelength λ: $I_s \propto \lambda^{-4}$.

The reflectivity $R(\omega, \theta)$ can easily be found by solving the Maxwell equations with suitable boundary conditions for an insulator film on a metal substrate. We shall seek the solution in the form $A=A(z)\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t)$, where $\mathbf{k}$ is the wave vector of an electromagnetic wave; the z axis is perpendicular to the film plane; the xy plane coincides with the surface of the metal substrate. For the p-polarized light, the reflectivity $R(\omega, \theta)$ is given by the expression

$$R=\left|\frac{\varepsilon(\omega)u\cos\theta-k_z v/k_0}{\varepsilon(\omega)u\cos\theta+k_z v/k_0}\right|^2, \qquad (2)$$

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where

$$u=\exp(-ik_zd)+(i\varepsilon_m(\omega)/\varkappa+\varepsilon(\omega)/k_z)\exp(ik_zd),$$
$$v=\exp(-ik_zd)-(i\varepsilon_m(\omega)/\varkappa+\varepsilon(\omega)/k_z)\exp(ik_zd),$$
$$k_z=k_0(\varepsilon(\omega)-\sin^2\theta)^{1/2},\quad \varkappa=k_0(\sin^2\theta-\varepsilon_{\text{м}}(\omega))^{1/2},$$

$k_0=\omega/c$ and $\varepsilon(\omega)$ and $\varepsilon_m(\omega)$ are the permittivities of the film and metal substrate at a frequency ω.

In the case when the substrate can be regarded as a perfectly conducting metal, so that $\varepsilon_m(\omega)\to\infty$, Eq. (2) becomes

$$R(\omega,\theta)=\left|\cos\theta+\frac{ik_z}{k_0\varepsilon(\omega)}\operatorname{tg}k_zd\right|^2\Big/\left|\cos\theta-\frac{ik_z}{k_0\varepsilon(\omega)}\operatorname{tg}k_zd\right|^2. \tag{3}$$

It has been shown earlier[4,8] that the optical properties of insulator films can be described satisfactorily by the permittivity of a bulk crystal, which has the following form in the quasiharmonic approximation:

$$\varepsilon(\omega)=\varepsilon_\infty+(\varepsilon_0-\varepsilon_\infty)\omega_{TO}^2/(\omega_{TO}^2-\omega^2+2i\omega\gamma). \tag{4}$$

In the case of thin films in the frequency range where $\varepsilon(\omega)$ is low and, consequently, $k_zd\ll 1$, Eq. (3) can be written in the form

$$R(\omega,\theta)=1-2\gamma\pi\frac{d}{\cos\theta}\sin^2\theta\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\omega_2^2\Big/[(\omega_2-\omega)^2+\gamma^2]. \tag{5}$$

A peak at the frequency ω_2 corresponds to the dipole vibrations of the film atoms, polarized at right-angles to the substrate, and it is identical with the frequency of longitudinal phonons in a bulk single crystal,[4,8] where $\varepsilon(\omega_2)\approx 0$. In this approximation we have $k_zd\ll 1$ and, bearing in mind that the substrate conductivity is finite, we find that Eq. (2) at $\omega\approx\omega_2$ becomes

$$R(\omega,\theta)=1-2\pi\gamma\frac{d}{\cos\theta}\sin^2\theta\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\omega_2^2/[(\omega_2-\omega)^2+\gamma^2]$$
$$+\frac{1}{\cos\theta\operatorname{Im}[-\varepsilon_{\text{м}}(\omega)]^{1/2}}. \tag{6}$$

If the permittivity of the metal is expressed in the form (see Ref. 10)

$$\varepsilon_m(\omega)=i\cdot 4\pi\sigma(\omega)/\omega, \tag{7}$$

where σ is the conductivity of the metal and if Eq. (7) is substituted into Eq. (6), it is found that

$$R(\omega,\theta)=1-2\pi\gamma\frac{d}{\cos\theta}\sin^2\theta\left(\frac{1}{\varepsilon_\infty}-\frac{1}{\varepsilon_0}\right)\omega_2^2/[(\omega_2-\omega)^2+\gamma^2]$$
$$-\frac{1}{\cos\theta}\left(\frac{2\omega}{\pi\sigma}\right)^{1/2}. \tag{8}$$

The last term in Eq. (8) describes the absorption of electromagnetic waves in a metal and it represents the well-known Hagen–Rubens correction.[10] It is clear from Eqs. (8) and (1) that the emissivity of a sandwich has, as in the $\sigma=\infty$ case, a Lorentzian peak at the frequency ω_2 and the half-width of this peak is γ. This peak is superimposed on the background, which rises smoothly with the frequency ω proportionally to $\omega^{1/2}$ and which is related to the emissivity of the metal.

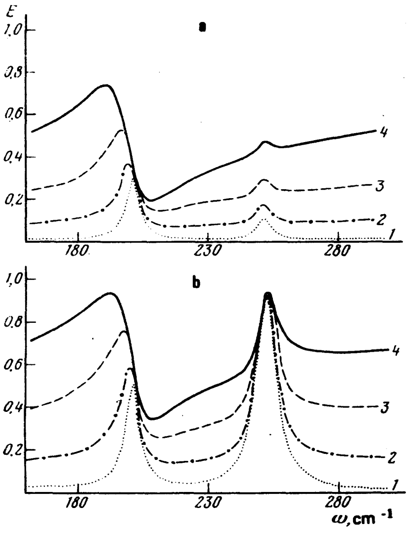

FIG. 1. Calculated emissivity of ZnSe films (1 μ thick) on metal substrates of various conductivities $\sigma(\Omega^{-1}\cdot\text{cm}^{-1})$: 1) 3×10^5 ($R=99\%$); 2) 6×10^3 ($R=93\%$); 3) 8×10^2 ($R=80\%$); 4) 150 ($R=55\%$); a) emission angle 15°; b) emission angle 60°.

In the frequency range of transverse optical phonons in the insulator film ω_{TO}, where $\varepsilon(\omega)$ is large, the approximation $k_zd\ll 1$ is invalid, the profile of the radiation peak ceases to be Lorentzian and depends strongly on the substrate conductivity. Figure 1 shows the frequency (ω) dependences of the emissivity of ZnSe films on metal substrates calculated on a computer using Eqs. (2), (4), and (7) for emission angles of 15 and 60°. In the investigated frequency range the conductivity of the metal substrates can be regarded as frequency-independent.

2. EXPERIMENTAL RESULTS AND DISCUSSION

We investigated the emissivity of zinc selenide films evaporated on aluminum, chromiun, and titanium substrates. A film of aluminum, chromium, or titanium about 5000 Å thick was first deposited in vacuum on glass and quartz substrates. The evaporation source was a tungsten boat. Homogeneous metal films with luster were obtained when the substrate temperature was 100–120°C. The rate of deposition did not exceed 20 Å/sec and the vacuum during deposition was $\sim10^{-6}$ Torr. The ZnSe films were deposited on such metal substrates under similar conditions: this was done by vacuum evaporation of compacted tablets made of a high-purity ZnSe powder. The selenide films were partly amorphous and required a further heat treatment. The degree of crystallinity of the ZnSe films was deduced from the intensity and half-width of the infrared emission bands and of the Raman scattering spectra. Prolonged recrystallization annealing in an argon atmosphere produced films whose peaks at the frequency ω_2 had half-widths close to the half-width of the function $\operatorname{Im}[-1/\varepsilon(\omega)]$ of a single crystal. The emissivity spectra of such films were compared with the calculated emissivity curves.

The emission spectra of the sandwiches were recorded and the emissivity was calculated by a method described earlier.[8] In this way we obtained, for example, the emissivity spectra of ZnSe films on aluminum mirrors (Fig. 2) for different angles of emission and two values of the thickness: $d=0.3\ \mu$ (Fig. 2a) and $d=1\ \mu$ (Fig. 2b). The emissivity of the sandwiches (dashed

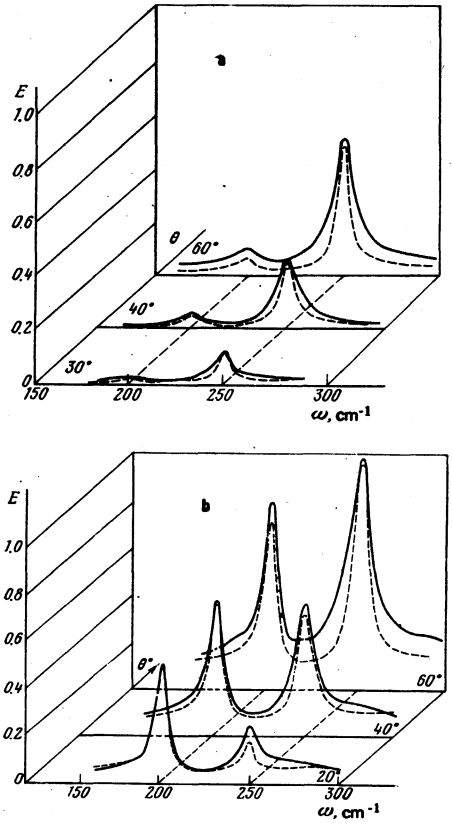

FIG. 2. Emissivity of ZnSe films on an aluminum mirror ($\sigma_{Al} = 2\times10^4\ \Omega^{-1}\cdot\text{cm}^{-1}$): a) ZnSe film thickness 0.3 μ; b) ZnSe film thickness 1 μ. The continuous curves are experimental and the dashed curves are calculated.

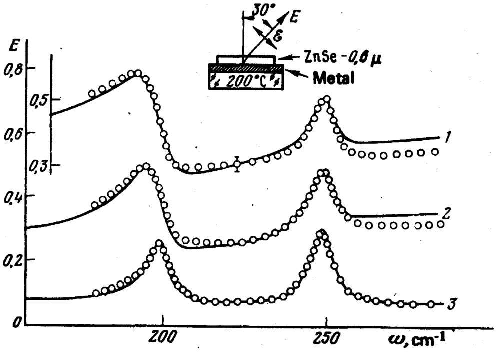

FIG 3. Emissivity of ZnSe films on titanium (1), chromium (2), and aluminum (3). The continuous curves are calculated and the points are the experimental data. The inset shows the experimental geometry: E is the direction of emission and $\mathscr{E}$ is the polarization of the emitted radiation.

curves) was calculated on a computer using Eqs. (2), (4), and (7) and substituting in the initial formulas the parameters of a ZnSe single crystal ($\omega_{TO} = 200$ cm^{-1}, $\gamma = 6$ cm^{-1}, $\varepsilon_0 = 8.9$, and $\varepsilon_\infty = 5.8$). The conductivity of the metal substrate was assumed to be $2\times10^4\ \Omega^{-1}\cdot\text{cm}^{-1}$, which corresponded to 96% reflectivity of the aluminum mirror in the investigated part of the spectrum. Bearing in mind the difference between the number of defects in films and single crystals (which affected particularly the half-widths of the absorption band), we concluded that the agreement between the experimental and calculated emissivities of sandwiches (Fig. 2) was satisfactory.

Figure 3 shows the emissivity of films 0.6 μ thick deposited on various metal substrates: aluminum, chromium, and titanium. All three samples were prepared in the same technological cycle and all of them were evaporated at the same time; this was followed by recrystallizing annealing in the same quartz ampoule. Therefore, we could assume that the degree of crystallinity of all three samples was the same. This was indicated by the identical half-widths of the high-frequency emission bands ($\omega_2 = 250$ cm^{-1}) of all three samples. The emissivity of these samples (continuous curves in Fig. 3) was calculated by substituting the experimental frequencies $\omega_1 = \omega_{TO}$ and ω_2, and the half-widths for a film on an aluminum mirror; the values of ε_0 and ε_∞ were taken to be the same as for a single crystal. The only variable was the substrate conductivity. The best agreement between the calculated and experimental values of the emissivity were obtained for $\sigma_{Al} = 8\times10^3\ \Omega^{-1}\cdot\text{cm}^{-1}$ ($R_{Al} = 94\%$), $\sigma_{Cr} = 5\times10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$($R_{Cr} = 76\%$), and $\sigma_{Ti} = 3\times10^2\ \Omega^{-1}\cdot\text{cm}^{-1}$ ($R_{Ti} = 67\%$).

It is clear from Fig. 3 that the theoretical calculations agree well with the experimental results. The small and trivial difference in the frequency range $\omega > 260$ cm^{-1} observed for the ZnSe films on chromium and titanium is clearly due to the fact that the substrate conductivity is no longer described satisfactorily by the Hagen–Rubens formula; in this spectral range the frequency dependence of the substrate conductivity is typical of a "poor" metal. The values of the chromium and titanium conductivity obtained in this way are in good agreement with the results of independent measurements of the conductivity of pure chromium and titanium films (in the absence of ZnSe). The conductivity of pure chromium and titanium films is only 15–20% higher than in sandwiches.

The above measurement and calculation method gives sufficiently reliable values of the conductivity of metal films in the infrared range even when these films are covered by an insulator layer and the traditional measurement methods are inapplicable. The metal is assumed to be in the bulk form but the calculation method is applicable also at frequencies such that the thickness of the metal film is considerably greater than the skin depth. In the opposite case, the measured conductivity of the film is underestimated (the case of thin metal films is considered in Ref. 4).

It follows from the theoretical calculations and experimental results that the low-frequency peak $\omega_1 = \omega_{TO}$ does not have a Lorentzian profile and its appearance depends strongly on the substrate conductivity. When this conductivity decreases, the peak is shifted toward lower frequencies and becomes broader. This behavior is evidence of a strong coupling between the conduction electrons in the metal substrate and the optical phonons (polaritons) near the center of the Brillouin zone of the thin insulator film. It follows from the polarization measurements of the emissivity and also from Refs. 8 and 9 that the low-frequency emission peak corresponds to the dipole vibrations of the film atoms polarized parallel to the substrate. The field of such a dipole penetrates into the metal and drags the conduction electrons. A reduction in the conductivity of the metal substrate enhances the transfer of energy from the dipole vibrations of the insulator "ions" to the metal and it shifts and broadens the low-frequency emission band.

Determination of the Raman spectra indicated that the influence of the conduction electrons in the metal substrate on the insulator polaritons in such sandwiches decreases rapidly on increase of the polariton wave vector. When this wave vector rises from 10^3 to 10^5 cm^{-1}, the shift and broadening of the low-frequency emission peak practically disappear.

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Study of orientational ordering of uniaxial liquid crystal by Raman-scattering spectroscopy

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A new procedure is proposed for the study of the orientational molecular ordering in uniaxial liquid crystals of *A*-smectic, nematic, and cholesteric type by laser Raman spectroscopy. Expressions are obtained from which to determine the coefficients of the expansion of the orientational molecular distribution function in powers of the experimental degrees of depolarization of the Raman scattering lines. The orientational molecular order in the nematic phase of methoxyamyltolane is investigated experimentally. It is shown that the anisotropy of the local field influences strongly the experimental results.

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1. INTRODUCTION

Combining the various types of orientational and translational molecular orders in the mesophase results in a large assortment of possible liquid-crystal structures.[1] Those of them which are optically uniaxial are the *A*-smectic, nematic, and cholesteric liquid crystals. For a quantiative description of the orientational ordering of the molecules in each of the indicated types of liquid crystals, we use the orientational distribution function $F(\varphi, \theta, \psi)$, which yields the probability of finding the orientation of the molecule in a small solid angle $d\Omega$ near the corresponding Euler angles φ, θ, and ψ (Ref. 2). These angles define the orientation of the molecular coordinate system relative to the laboratory frame. In nematic and *A*-smectic liquid crystals, the z axis is chosen to coincide with the director $\mathbf{r}$, and the x and y axes are in a plane perpendicular to it. In the quasinematic layer of the planar texture of a cholesteric liquid crystal, the z axis coincides with the director $\mathbf{r}_c$ of the layer, the x axis lies in the plane of the layer, and y is perpendicular to the layer. X-ray structure data[1,3,4] show that the directions $\mathbf{r}$ and $(-\mathbf{r})$ in nematics and *A*-smectics are equivalent. The same