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Influence of photon-phonon interaction on the optical properties of aluminum powder

© A.I. Kiselev, V.G. Shevchenko, A.V. Konyukova

Institute of Solid State Chemistry, Russian Academy of Sciences, Ural Branch,
620108 Yekaterinburg, Russia

e-mail: kis1771@yandex.ru

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By comparing the simulated and experimental optical conductivity, the electronic structure of the aluminum film and powder at room temperature was studied. The main attention is paid to the region of the optical conductivity spectrum at absorbed photon energies above 1.3 eV. It is assumed that in this section the form of the optical conductivity spectrum of aluminum powder is largely determined by the processes of heat release during photon-phonon interaction. From a comparison of the electronic characteristics of the spectra of the film and aluminum powder, the lower limits of the forbidden band of optical phonons of the metal-oxide interface are presumably established.

Keywords: phonons, ellipsometry, optical properties of the film, electronic characteristics of optical transitions

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Introduction

It is known that the study of the processes of heat release during photon-phonon interaction is performed by phononics i.e.actively developing branch of physics that studies the propagation of elastic oscillations in media with a complex periodic structure. The name of this area has something in common with electronics and photonics i.e. the science of accurate, sometimes even „per-photon“, control of light flows. The analogy doesn't end there. In phononics, some technical devices and methods of theoretical description are used, which were borrowed from these two branches.

Note the fact that phononics is a branch of physics that deals with the fine control of sound, ultrasonic and thermal vibrations in various structures. Unlike acoustics, an active role is played here the medium itself through which the vibration propagates. At the same time, by analogy with the spectrum of electromagnetic waves, several frequency ranges are distinguished in the spectrum of elastic vibrations: infrasound, sound, ultrasound, hyper-sound and heat. Elastic vibrations with frequencies of the order of a terahertz and higher are referred to as thermal vibrations. The wavelengths of such vibrations approach interatomic distances, and the discrete nature of matter limits this scale from above.

At present, it has been possible to manufacture an acoustic diode i.e. device that transmits a sound wave only in one direction. In this case, the answer to the question of how to make the medium play an active role in controlling the flow of sound waves is the transmission of sound through a material with regularly alternating mechanical properties. This regularity can be either strictly periodic or periodic, but with modulation : the main thing is that the alternation period be small. If it is comparable to the wavelength of a sound wave, then a phononic crystal is obtained, which is the key element of an acoustic diode. An obvious area of application for such a diode is preventing the reflection of sonar radiation, with the help of which submarines are detected.

At present, thanks to phononics, it has become possible to manufacture devices in which acoustic and optical vibrations are simultaneously contained. Interactions between elastic vibrations and a light wave are easily tuned and can be used, for example, for microscopic radio wave diagnostics of elastic waves [1].

Much more difficulties are caused by an attempt to transfer all the achievements described above to the field of thermal vibrations, i.e., for frequencies by the order of terahertz and higher. In particular, if a sound wave can be described using a single frequency, then thermal phonons usually exist in a solid at once in a very wide range of frequencies. This further complicates their control, since acoustic devices are usually only optimized for a certain frequency range.

The purpose of this work is to refine the lower limit of the frequency of thermal phonons produced by the interaction of photons and optical phonons at the interface between oxide and metal of aluminum powder. The existence of optical phonons requires at least a two-component medium. For the oxide−metal interface, two such systems can be considered: an ion in the bulk of the metal−atom on the surface and an atom on the surface−metal atom in the oxide.

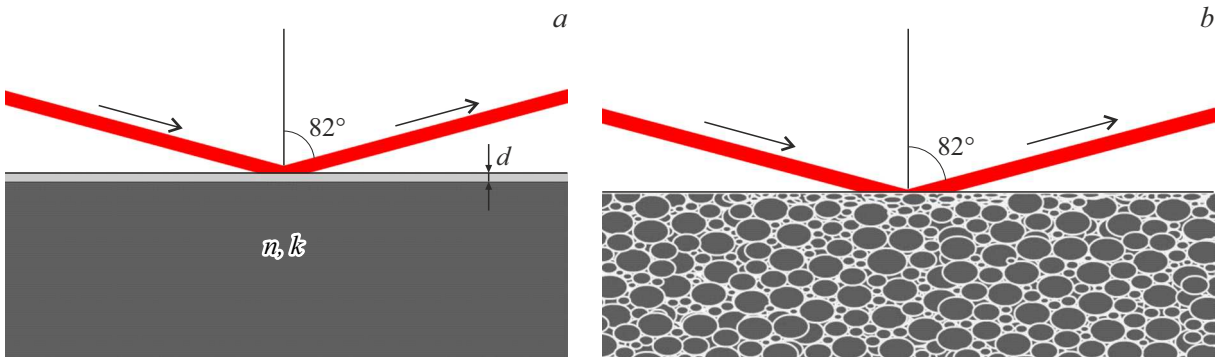

Figure 1. Surface model of aluminum film (a) and pressed powder (b).

Table 1. Spectral dependence of optical constants of ASD-4 at 298 K

$\hbar\omega$, eV	n	k	$\hbar\omega$, eV	n	k	$\hbar\omega$, eV	n	k
0.50	10.14	2.48	0.95	8.39	6.28	1.88	3.74	6.57
0.52	10.20	2.68	1.03	7.64	6.72	1.94	3.36	6.45
0.54	10.34	2.86	1.13	6.75	6.90	1.97	3.13	6.47
0.56	10.30	3.12	1.24	5.77	6.73	2.00	2.96	6.40
0.59	10.34	3.35	1.27	5.62	6.73	2.07	2.64	6.25
0.62	10.25	3.50	1.55	5.10	6.25	2.14	2.37	6.24
0.65	10.30	3.66	1.59	4.95	6.32	2.21	2.17	6.13
0.69	10.27	3.87	1.63	4.82	6.36	2.30	1.93	5.96
0.73	10.09	4.47	1.68	4.69	6.33	2.38	1.76	5.81
0.78	9.84	4.92	1.72	4.47	6.32	2.48	1.55	5.50
0.83	9.67	5.38	1.77	4.21	6.40	2.58	1.41	5.32
0.89	9.23	5.73	1.82	4.05	6.52			

Experiment procedure

To determine the characteristics of aluminum, thin polycrystalline films were prepared by deposition of aluminum grade A000 in a vacuum of about 0.1 Pa on the lower face of a glass prism. This process was performed by vacuum thermal evaporation in VUP-5M vacuum universal station using a tungsten evaporator. The film thickness is about 1 μm. Powder ASD-4 (Aluminum spherical, dispersed) with a predominant particle diameter of 5–10 μm was used to study the powders The samples were pressed into tablets 13 mm in diameter (0.7 g of powder, compression-moulding pressure 40 kg/cm^2). In this case, the surface of the tablet under study mirrored the polarized light emission.

The experimental dependences were obtained by the Beatty ellipsometric method (LEF-3M ellipsometer, spectral range 0.4–2.5 μm, angle of incidence of the light beam on the sample $\varphi = 82°$). From ellipsometric parameters Δ and ψ, the optical constants of pressed powder and bulk aluminum were calculated using the following equations:

$$n^2 - k^2 = n_0^2 \sin^2\varphi_0 \left[1 + \mathrm{tg}^2\varphi_0 \frac{\cos^2 2\psi - \sin^2 2\psi \sin^2\Delta}{(1 + \sin 2\psi \cos\Delta)^2}\right], \quad (1)$$

$$2nk = n_0^2 \sin^2\varphi_0 \,\mathrm{tg}^2\varphi_0 \frac{\sin 4\psi \sin\psi}{(1 + \sin 2\psi \cos\Delta)^2}, \quad (2)$$

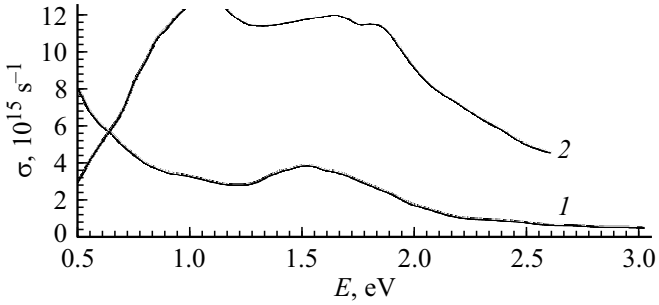

Figure 2. Optical conductivity spectrum of aluminum ($T = 298$ K): *1* is aluminum film, *2* is spectrum of pressed ASD-4 powder.

where n is the refraction index of the sample, k is the absorption coefficient, n_0 is the refraction index of the environment (in this case, the environment is air, $n_0 = 1$), Δ is relative phase difference for p- and s-components of electromagnetic waves reflected and incident on the sample, $\mathrm{tg}\,\psi$ is ratio their amplitudes. The measurement error of optical constants did not exceed 5% in the visible range of the spectrum, was 8% in the IR region.

Results and discussion

The spectral dependence of the optical constants n and k of an aluminum film at 298 K was obtained in the work [2]. Table 1 shows the dependences of the optical constants for the ASD-4 powder in the photon energy range from 0.5 to 2.58 eV Data on optical constants for ASD-4 powder were obtained for the first time. Fig. 1 shows models of ellipsometric experiments for film surfaces and pressed aluminum powder. A comparison of the optical constants for the pressed ASD-4 powder with those obtained earlier for aluminum [3] showed that at relatively close absorption coefficients, the values of the refraction index of the aluminum powder are significantly higher. The optical conductivity spectra σ of the film and pressed powder obtained from these optical constants are shown in Fig. 2.

The characteristics of the electronic states that form the optical conductivity spectra were determined by minimizing the deviation of the experimental optical conductivity spectra from the model spectra [4]. When constructing the model spectrum, each contribution of the photon absorption process was taken into account graphically using the position for the photon absorption peak (photon energy $E = \Delta_j = \hbar\omega_j$), peak height (coinciding with the frequency of plasma vibrations ω_{Pj}) and its half-width (i.e., the relaxation frequency ω_{0j}). Here j is the number of the contribution. From the summation rule for the frequencies of plasma oscillations, the statistical average of the number of electrons z_j involved in the formation of contributions to the optical conductivity is estimated.

Contributions to optical conductivity from electrons, that is in different energy states, are additive [5]. Let's represent the expression for the spectrum of light conductivity in the form

$$\sigma(\omega) = \sum_{j=0}^{n} \sigma_j(\omega), \tag{3}$$

where n — is the total number of bands of in-band and interband transitions. Index $j = 0$ refers to the band of conduction electrons, and the rest ones refer to the bands of interband transitions. With the help of the equation for conduction electrons (Drude-Zener model):

$$\sigma_0(\omega) = \frac{1}{4\pi} \frac{\omega_{p0}^2 \omega_{00}}{\omega^2 + \omega_{00}^2}, \tag{4}$$

the acceleration of electrons inside the conduction band is taken into account. This contribution, written as the approximations of the Drude approach, can take part in the formation of the optical conductivity spectrum over the entire studied photon energy range.

Contributions from interband transitions:

$$\sigma_j(\omega) = \frac{1}{4\pi} \frac{\omega_{pj}\omega^2\omega_j\omega_{0j}}{(\omega^2 + \omega_{0j}^2)^2} \left(\frac{\omega^2 - \omega_{0j}^2}{A_j B_j} - \frac{2B_j}{A_j} + \frac{2}{\omega_j} \right), \tag{5}$$

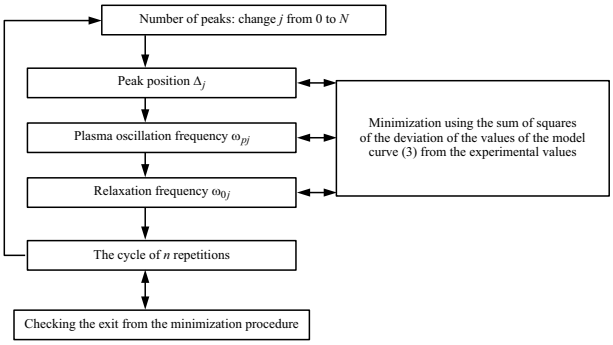

Figure 3. Block diagram of the minimization procedure.

where ω_j is the position of the interband transition peak on the curve $\sigma(\omega)$,

$$A_j = \sqrt{z_j^2 + 4\omega^2\omega_{0j}^2},$$

$$B_j = \sqrt{(A_j + z_j)/2}, \quad z_j = \omega_j^2 - \omega^2 + \omega_{0j}^2,$$

in graphical representation they have a bell-shaped form. All the while takes into account their asymmetry due to the surface dispersion of light [6].

When processing the results of the experimentally measured light conductivity, the classical Drude-Zener part (4) is initially subtracted, which is determined by the contribution from almost free electrons of the conduction band. The remaining contributions are interpreted using several additive functions (5). A block diagram of varying the parameters of the model optical conductivity to minimize its deviation from the experimental one is shown in Fig. 3. When varying the optical conductivity parameters, for each parameter value, the sum of the squared deviations of the experimental and model optical conductivity was determined for the photon energies in the entire experimental range. Later, the position of the minimum of these sums was determined, from which the resulting value of the parameter was found. In the work [4] the example of step-by-step implementation of such a variability is given.

The purpose of the minimization procedure is to determine the necessary and sufficient number of functions (5). When the minimization procedure is running, a stage occurs when the inclusion of a peak with the number $N + 1$ causes the appearance of negative values of the plasma oscillation frequency during the cycle of variability the parameters of the model optical conductivity. This stops the minimization procedure and, as a result, the parameters of the model optical conductivity for N peaks are fixed.

The results of using the minimization procedure for the experimental optical conductivity spectra of the aluminum film and pressed powder, presented in Table 2, showed that the conduction band is splitted. The conduction band in the aluminum film is represented by the contributions with j equal to 0 and 1, as well as for the ASD-4 powder. The distribution of electrons during the splitting

Table 2. Electronic-characteristics of the model optical conductivity of aluminum film and powder at 298 K

Aluminum-film					ASD-4,pressed powder				
j	Δ_j, eV	$\omega_{pj} \times 10^{-15}, s^{-1}$	$\omega_{0j} \cdot 10^{-15}, s^{-1}$	z_j	Δ_j, eV	$\omega_{pj} \times 10^{-15}, s^{-1}$	$\omega_{0j} \cdot 10^{-15}, s^{-1}$	z_j	
0	0	1.4881	0.8609	0.0116	0	0	0.0000	0.0000	0.0010
1	0.4278	7.3550	0.0984	0.2823	1	0.5950	9.8046	0.3506	0.5017
2	0.6138	2.7690	0.0897	0.0400	2	0.7317	2.0556	0.0307	0.0221
3	0.7236	1.7476	0.0683	0.0159	3	0.8144	5.1596	0.0968	0.1389
4	0.8525	1.9469	0.0612	0.0198	4	0.9143	5.0561	0.1038	0.1334
5	0.9620	1.9106	0.0300	0.0191	5	1.0057	5.4066	0.1119	0.1526
6	1.0559	1.9157	0.0443	0.0192	6	1.1025	5.5917	0.1285	0.1632
7	1.1343	1.1821	0.0179	0.0073	7	1.2300	4.0855	0.1329	0.0871
8	1.2090	1.8412	0.0169	0.0177	8	1.3243	4.4493	0.0926	0.1033
9	1.2745	1.4953	0.0189	0.0117	9	1.4145	3.4730	0.0378	0.0629
10	1.3073	1.3887	0.0159	0.0101	10	1.5061	4.1042	0.0582	0.0879
11	1.3553	2.0751	0.0119	0.0225	11	1.5970	5.4480	0.1064	0.1549
12	1.4040	2.0445	0.0262	0.0218	12	1.6800	4.5367	0.1031	0.1074
13	1.4562	2.4845	0.0308	0.0322	13	1.7972	4.9106	0.1000	0.1259
14	1.5182	2.5946	0.0293	0.0351	14	1.8597	3.6569	0.0912	0.0698
15	1.6047	2.1782	0.0306	0.0248	15	1.9438	1.5577	0.0891	0.0127
16	1.6852	1.9746	0.0324	0.0203	16	2.1642	2.6894	0.1234	0.0377

of the conduction band is reflected in the behavior of the frequencies of plasma oscillations In this case, the frequencies ω_{Pj} with $j = 0$ (the contribution to the optical conductivity written in the framework of the Drude model) are minimal or equal to zero.

The concept of the splitting of the conduction band of mercury in the liquid state was introduced by Mott in the work [7]. The reason for the significant discrepancy between the experimental data on electrical conductivity and the model estimates of the Drude approach was explained by him through significant decrease in the density of states in the region of the Fermi surface in the energy spectrum of mercury electrons. The results of the work [8] confirmed Mott's hypothesis about the presence of a pseudogap in the energy spectrum of mercury.

The characteristics of electrons in bands with j equal to 3, 4, and 5 for aluminum and for powder refer to surface states. Here, the bands directly adjacent to the conduction bands are formed by interband transitions of electrons in surface states. In the work [9], it is shown that the number of electrons of surface states in the powder is several times greater than in the aluminum film. Their influence on the plasma frequency of surface states forms a significant difference too between the optical conductivity spectra of the film and powder in the region of 1.1 eV.

In the high-energy region, the type of optical conductivity of the aluminum powder is determined by the characteristics of the presumably photon-phonon interaction centered near the photon energy of 1.8 eV. The existence of optical phonons requires at least a two-component medium. For the oxide−metal interface, two such systems can be considered: an ion in the bulk of the metal-atom on the surface and an atom on the surface−metal atom in the oxide.

Conclusions

Note the fact that for the powder the relaxation frequencies ω_{0j}, which are responsible for the width of the transition band, are significantly higher than for the film.

Contributions to optical conductivity with numbers $j = 8$, 9, 10 and $j = 13$ (results for an aluminum film) most likely correspond to the region of forbidden bands between acoustic and optical phonons for two subsystems: an aluminum ion in a metal−atom on the surface and aluminum atom on the surface−atom in the oxide. The energy states of these forbidden bands can be determined by the values 1.25 and 1.45 eV.

The increase in optical conductivity indicates the fact of more intense absorption of incident photons, whose energy is transferred to thermal phonons and local heating occurs at the metal-oxide interface.

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Conflict of interest

The authors declare that they have no conflict of interest.

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