Brillouin Scattering from Surface Phonons in Al-Coated Semiconductors

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Brillouin spectra from thermally excited surface acoustic phonons in GaAs and Si surfaces coated with a thin Al film are presented. The measurements show features different from the Al and the semiconductor surfaces. We are able to give a theoretical explanation of the experimental results in terms of the coupling between the normal modes of the film and of the substrate.

The study of the surface-phonon spectrum is receiving increasing attention because of the inelastic light-scattering techniques—Brillouin scattering—which allow an accurate determination of the long-wavelength part of the spectrum.[1] The interaction of the light with the surface takes place through two different mechanisms according to the optical absorption coefficient of the medium. If the medium is partially transparent (semiconductors below the absorption edge) the Brillouin cross section is dominated by the coupling between the light and the variations of the dielectric susceptibility of the medium induced by the phonons.[2,3] This is the elasto-optic effect. Conversely, for highly absorbing materials (metals) the cross section is due to the surface ripples induced by the displacement component normal to the surface.[4-6]

Until now the theoretical[2,4] and experimental[1] investigation has given evidence of both mechanisms in clean surfaces. The only attempt to study surface phonons in a system with an interface has concerned two transparent media.[7] In this case, however, only the localized states (Rayleigh and Sezawa waves) were considered.

In this work we will investigate the whole acoustic surface-phonon spectrum of a thin metallic film deposited over semiconductor substrates. We make use of incident light of 5145 Å so that the large value of the optical absorption coefficient of Al does not allow the light to interact appreciably with the semiconductor substrate. As already remarked, for metal surfaces the ripple mechanism is dominant and one would expect to obtain metal-type spectra.[4] We will show instead that the presence of the interface does modify qualitatively the surface phonons in the film.

The measurements were made by using the Brillouin-scattering technique and the experimental apparatus previously employed for clean surfaces.[1] A backscattering arrangement was used with the incident light wave vector $\vec{k}$ making an angle θ to the surface normal of the sample. Because of wave-vector conservation on the surface, the light interacts with phonons having parallel momentum $Q = 2k \sin\theta$. The polarization of the light was chosen in the plane of $\vec{Q}$ and $\vec{k}$. The experiments were performed in air at room temperature. The presence of an oxide layer (of about 20–30 Å) over the Al surface does not affect the measurements because the thickness of the oxide layer is much smaller than the wavelength of the phonons excited by the light.

In Figs. 1 and 2 are shown the experimental spectra for Si and GaAs substrate, respectively, coated with an Al film. We have considered the (001) surface of Si with $\vec{Q}$ along the [100] direction. The light incidence angle was $\theta = 73°$ and the coverage about 400 Å thick. In the case of GaAs the surface orientation was (110) and $\vec{Q}$ was chosen along the $[1\bar{1}0]$ direction with $\theta = 70°$. The Al film was about 300 Å thick.

It appears clearly from Figs. 1 and 2 that these results are completely different from those in pure Al.[1] Furthermore, the spectra cannot be explained in terms of the substrate displacement components normal to the surface.[2,3] In particular in the observed spectra there are important structures localized at the transverse threshold Ω_T of the substrate and the longitudinal threshold

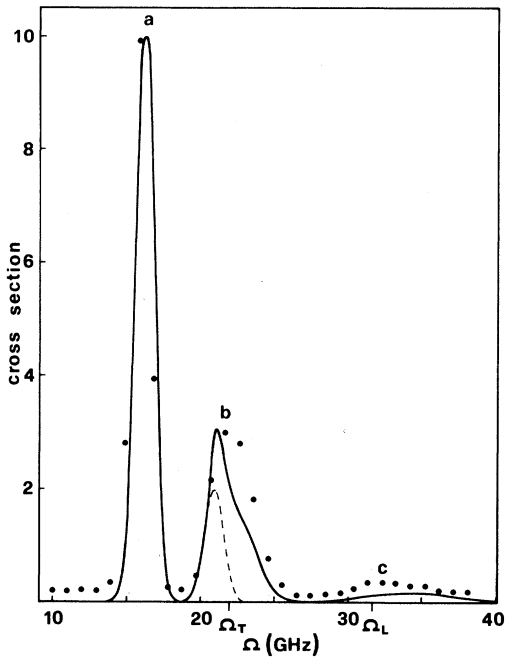

FIG. 1. Brillouin spectrum of (001) Si coated with Al. Dots: experimental points. Full line: theoretical cross section. The area under the dashed line indicates the contribution arising from the second-order Sezawa wave.

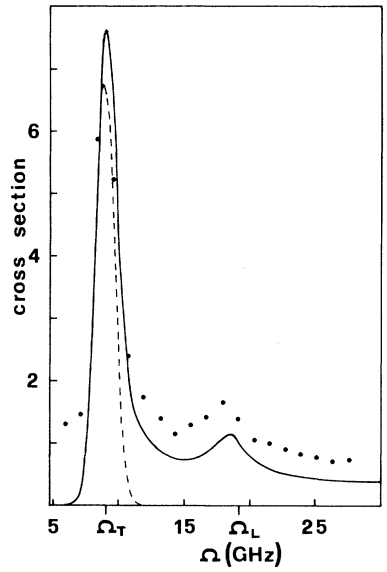

FIG. 2. Brillouin spectrum for (110) GaAs coated with Al. Dots: experimental points. Full line: theoretical cross section. The area under the dashed line indicates the contribution arising from the Rayleigh wave. In this case the reference system has been chosen with the x axis pointing along the crystallographic [110] direction and the z axis along the [1$\bar{1}$0] direction.

Ω_L.[8] In GaAs—Fig. 2—there is a well defined peak at Ω_L, while in Si—Fig. 1—a pronounced peak is present near Ω_T. The low-frequency peaks present in both the spectra correspond to localized modes (Rayleigh and Sezawa waves). The experimental spectra at high frequency, not shown in Figs. 1 and 2, do not present any structure. We remind the reader that at these frequencies clean semiconductor surfaces show peaks due to the elasto-optic coupling with bulk phonons.[1] The complete flattening of our spectra in this region indicates that the light interacts only with the Al film, at the coverage considered.

In order to explain the behavior of the experimental spectra we have performed a calculation of the displacement field for a semi-infinite anisotropic semiconductor substrate covered with an isotropic film representing the polycrystalline Al. Let us consider the substrate in the half-plane $z < 0$ with the surface in the x-y plane and the slab of thickness d in the region $0 < z < d$. At the surface ($z = d$) we impose (i) the free stress boundary conditions while at the interface ($z = 0$) we have to impose (ii) the continuity of the displacement field and (iii) the balance of the pressure. In our measurements the scattering is confined in the sagittal plane.[9] Furthermore, in the cases under consideration the normal modes in the sagittal plane are decoupled from the shear mode orthogonal to it. Therefore only the displacements with longitudinal (l) and transverse (t) polarization lying in the sagittal plane have to be considered.

In the Al region the displacement field at fixed parallel momentum $\vec{Q}$ and frequency Ω is given by

$$\vec{u}(\vec{Q},\Omega,z) = \exp[i(\Omega t + \vec{Q}\cdot\vec{R})][a(q_l)\vec{v}(q_l)\exp(iq_l z) + a(-q_l)\vec{v}(-q_l)\exp(-iq_l z) + a(q_t)\vec{v}(q_t)\exp(iq_t z) + a(-q_t)\vec{v}(-q_t)\exp(-iq_t z)] \quad \text{for } z < 0 < d. \tag{1}$$

Here $\vec{R}$ is the position vector on the surface and $q_{l,t}$ are the z components of the momentum satisfying the Al phonon dispersion relations at fixed $\vec{Q}$ and Ω. The two-dimensional vectors $\vec{v}$ represent the normal modes of Al associated with $q_{l,t}$.

In the substrate region the displacements have the form

$$\vec{u}(\vec{Q},\Omega,z)=\exp[i(\Omega t+\vec{Q}\cdot\vec{R})][b(q_l)\vec{v}(q_l)\exp(iq_lz)+b(-q_l)\vec{v}(-q_l)\exp(-iq_lz)+b(q_t)\vec{v}(q_t)\exp(iq_tz)+b(-q_t)\vec{v}(-q_t)\exp(-iq_tz)] \quad \text{for } z<0. \tag{2}$$

The z component of the momentum $q_{l,t}$ satisfies here the phonon dispersion relations of the semiconductor and the $\vec{v}$'s are the associated eigenvectors. In the semi-infinite medium only the $q_{l,t}$'s with $\mathrm{Im}(q_{l,t})\leq 0$ have to be retained. In the Al region, instead, we must consider all the complex solutions $q_{l,t}$, which represent both decaying and growing waves inside the film.

The arbitrary constants a's and b's are determined by the system of equations representing the boundary conditions. These conditions, (i), (ii), and (iii), written for the components of the two-dimensional displacements—Eqs. (1) and (2)—give rise to a system of six linear equations in the unknowns a's and b's. In the film all the waves are allowed for any range of energy so that we have four a's. In the substrate, for $\Omega<\Omega_T$, there are two decaying waves and we must set $b(-q_l)=b(-q_t)=0$. In this case the system is homogeneous and the vanishing of the determinant gives rise to the localized solutions, as the Rayleigh and Sezawa waves. Between Ω_T and Ω_L the transverse wave of the substrate becomes real so that $b(-q_l)=0$. There are seven unknowns and the solutions of the inhomogeneous system give rise to the continuous part of the spectrum. Above Ω_L both the phonon branches are real. The unknowns a's and b's numbering now eight, there are two independent solutions representing two degenerate displacements. We label by the index j these solutions, which must be diagonalized.

The Brillouin cross section from surface ripples, which is proportional to the thermal-averaged mean-square displacements normal to the surface, can be written in backscattering geometry as[4,10]

$$I(\Omega)=\frac{k_B T}{2\pi^2\rho\Omega^2}k^4\cos^3\theta\sum_j\left|u_z{}^j(\vec{Q},\Omega,z=d)\right|^2, \tag{3}$$

where $u_z{}^j$ is the z component of the displacements of Eq. (1), evaluated at the surface, and ρ is the density of Al. In the calculations we have used the known values of the elastic constants of Si, GaAs, and Al.[11] In order to compare the experimental spectra directly with the calculations we have convolved the theoretical cross section—Eq. (3)—with a Gaussian representing the instrumental resolution function. The arbitrary constant between the intensity of the theoretical and experimental spectra has been chosen to make equal the heights of lower-frequency peak. The final theoretical curves are compared with the experimental data in Figs. 1 and 2.

Let us first discuss the results for Si displayed in Fig. 1. Our calculations show a Sezawa wave localized at $\Omega=16.2$ GHz, in good agreement with the experimental peak at 15.9 GHz (structure a). This is a Sezawa wave instead of a Rayleigh wave because its velocity (4367 m/sec) is greater than the shear-wave velocity in Al (2931 m/sec).[12] Notice the large frequency shift of this localized state with respect to the Rayleigh wave in clean Si (18.3 GHz). The second structure (b) represents something new with respect to the previous measurements in clean surfaces.[1] Our calculations indicate that this large peak localized near the longitudinal threshold ($\Omega_T=21.7$ GHz) arises from surface modes of two different kinds. The left-hand side of this structure is due to a second-order Sezawa wave ($\Omega=20.9$ GHz), while the shoulder which appears on the right-hand side is due to a continuum of modes having surface character. These modes arise from shear vibrations of the substrate which reach the film surface amplified, retaining the z-transverse polarization. This occurs because the boundary conditions at the interface couple the film and substrate displacements of Eqs. (1) and (2). The third structure (c) near Ω_L, which is present in both the experimental and calculated intensities, is reminiscent of the longitudinal modes in the substrate, strongly peaked in this region.[2,3] These vibrations reach the surface with a mixed longitudinal and z-transverse polarization.

We turn now to discuss the GaAs results of Fig. 2. In this case the experimental surface structures are superimposed on a fairly large background. The localized state is a true Rayleigh wave whose frequency $\Omega_R=8.9$ GHz is only slightly shifted with respect to the Rayleigh wave of the substrate (8.8 GHz). The transverse threshold ($\Omega_T=9.1$ GHz) is very close to Ω_R so that the structure associated with the shear modes at Ω_T cannot be resolved from the Rayleigh peak. However, the effect of the modes belonging to the continuum is noticeable even in this case.

The other structure at Ω_L is accounted for in

terms of the very large longitudinal displacements of (110) GaAs,[2] which at the film surface show a mixed longitudinal and z-transverse polarization. We have found previously[2] that this structure is present also in the clean GaAs spectrum at the same frequency Ω_L. However, we want to stress that in the case of the clean surface the peak is due to the elasto-optic coupling while the Al cover causes the peak to originate from the ripple mechanism.

In conclusion, by describing the interaction of the light with the metallic film through the ripple mechanism and by using the theory of elasticity for the displacement field, it is possible to reproduce the surface features of both the continuous and the discrete part of the Brillouin spectrum. Our analysis indicates the existence of a strong interaction between the long-wavelength modes in the two media.

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Conductivity of the One-Dimensional Conductor Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) near Commensurability

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We report an important drop in the longitudinal conductivity of TTF-TCNQ occurring at constant temperature in the metallic phase and in a narrow pressure domain located around 19 kbar. The drop of conductivity has been related to a $\times 3$ commensurability of the longitudinal distortion with the lattice. This experiment, together with x-ray diffuse scattering of TTF-TCNQ could suggest that a significant fraction of the metallic conductivity below ambient temperature is due to the fluctuating collective mode.

The organic conductor TTF-TCNQ exhibits several experimental features characteristic of one-dimensional (1D) metallic behavior.[1,2] Large values of electron-electron interactions in TTF-TCNQ are necessary for the interpretation of the enhancements observed in spin susceptibility[3] and nuclear relaxation rate.[4] However, the electron-phonon interaction reveals its presence through the existence of structural phase transitions at low temperature.[5] Understanding of the metallic conductivity remains the main puzzle for TTF-TCNQ and its derivatives. Various theories have been proposed for the resistivity: (a) the single-particle scattering picture: intramolecular phonon scattering,[6] second-order scattering against librations,[7] interchain electron-electron scattering,[8] electron-spin fluctuation scattering[9]; (b) the collective-mode picture: important contribution from fluctuating charge-density waves.[10-12] The study of the TTF-TCNQ

