PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Inelastic scattering of low-energy electrons from Sn overlayers on cleaved InSb(110) surfaces

A. Ritz and H. Lüth
II. Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule Aachen, D-5100 Aachen, Federal Republic of Germany
(Received 3 June 1985)

Room-temperature deposition of Sn onto a clean, cleaved InSb(110) surface results in homogeneous layers of amorphous or polycrystalline α-Sn with tetrahedral sp^3-bonding order and semiconducting properties. Layers with a thickness exceeding about 500 Å grow in the metallic β-Sn modification. High-resolution electron-energy-loss spectroscopy (HREELS) is used to study the electronic properties of the Sn overlayers. Coupled interface plasmons of the Sn/vacuum and the Sn/InSb(110) interfaces are found near loss energies of 70 and 50 meV, respectively. In addition, a significant monotonic loss background due to the free electrons in the Sn layer develops, reaches its maximum at a film thickness of about 30 Å, and decreases again. A consistent theoretical description in terms of dipole scattering (dielectric theory) on a layered electron plasma (Sn layers) on top of an infrared-active semiconductor (InSb) is possible. The analysis allows the determination of transport parameters for the Sn overlayers.

I. INTRODUCTION

Inelastic scattering of low-energy electrons [usually the method is called high-resolution electron-energy-loss spectroscopy (HREELS)] has been proven to be an ideal experimental technique to study low-energy electronic excitations on semiconductor surfaces,[1,2] in addition to its application as a vibrational spectroscopy for adsorbed molecules. With respect to the problem of Schottky barriers on III-V semiconductor surfaces it has also recently been shown that HREELS can yield information about the space-charge layer underlying an adsorbate or a monolayer metal film.[3] The present work is intended to check the possibilities and benefits of using HREELS for studying metal overlayers and heterostructures by means of their collective and single particle excitations. It is, in particular, interesting to see how the loss spectrum of an infrared active III-V semiconductor, such as InSb, is modified by the presence of a conducting overlayer as its thickness passes from the limit of zero coverage, through two-dimensional film formation, and then on to bulk growth.

The system Sn on InSb(110) has been chosen for the investigation since, based on recent studies,[4,5] a lot of information is available about the structural, chemical, and morphological nature of these films. On a clean cleaved InSb(110) surface and up to a thickness of about 500 Å the Sn film grows homogeneously, layer by layer, in an amorphous or polycrystalline α-Sn—like modification. The Sn layer is semiconducting rather than metallic; the tetrahedral sp^3 bonding configuration is found, but no long-range crystalline order is revealed. After reaching a film thickness of about 500 Å further Sn deposit changes into the metallic β-Sn structure, which is the commonly stable modification at room temperature. For the monolayer regime and for layer thicknesses of a couple of hundred angstroms, a well-defined system is therefore given which resembles more a semiconductor heterostructure than a metal/semiconductor junction. This in particular is interesting since the results on this heterostructure can be compared with recent HREELS studies on metal/semiconductor systems [Ag/Si (111) (Ref. 6), Ag/GaAs(110) (Ref. 7)].

II. EXPERIMENTAL

Experiments were carried out at room temperature in an ultrahigh-vacuum (UHV) chamber which was pumped by ion pumps in combination with a titanium sublimator (base pressure: $p < 10^{-8}$ Pa). The electron-energy-loss spectra were recorded by means of a spectrometer with two electrostatic 127° deflectors as monochromator and analyzer. The energetic resolution of the spectrometer is about 7 meV.

The monocrystalline InSb samples were prism shaped ($10\times5\times5$ mm^3) with grooves for cleavage along [110] direction. Cleaving in UHV was achieved by means of the double-wedge technique. The InSb material was undoped with a free-carrier concentration of about 2×10^{16} electrons/cm^3, essentially the intrinsic concentration of InSb at room temperature.

The Sn (Ventron) had a purity of 99.999 95% in regard to metallic impurities. During evaporation of the Sn from an electrically heated Mo filament, the pressure stayed in the 10^{-8} Pa region. The coverage measured by a quartz balance is expressed in monolayers [1 monolayer (ML)$=6.7\times10^{14}$ atoms/cm^2 related to InSb(110)].

III. RESULTS

Loss spectra of the clean cleaved InSb(110) surface and after deposition of Sn layers with differing thickness are shown in Fig. 1. The measurements were performed under specular reflection with an angle of incidence of 80° and a primary energy of 20 eV. On the clean surface the loss and gain energy range between -30 and $+30$ meV is characterized by a broad structure consisting of the elastic

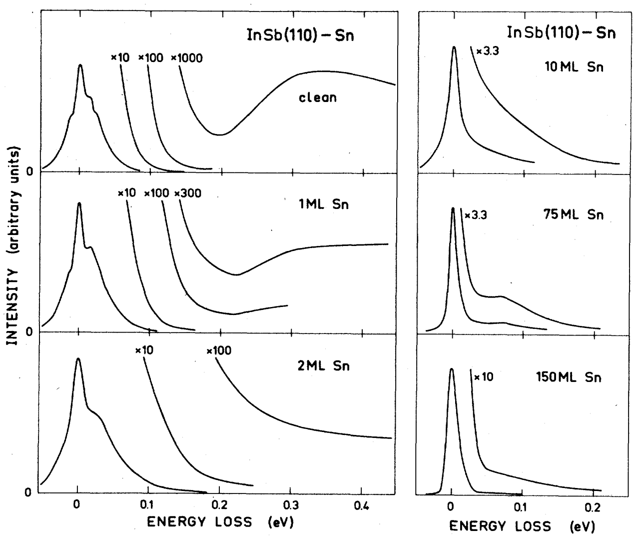

FIG. 1. Loss spectra (primary energy $E_0=20$ eV, specular reflection $\theta=80°$) of a clean cleaved InSb(110) surface and after deposition of Sn layers with increasing thickness. One monolayer (1 ML) corresponds to 6.7×10^{14} atoms per cm^2. The amplification factors given at the spectra are with respect to the elastic peak intensity.

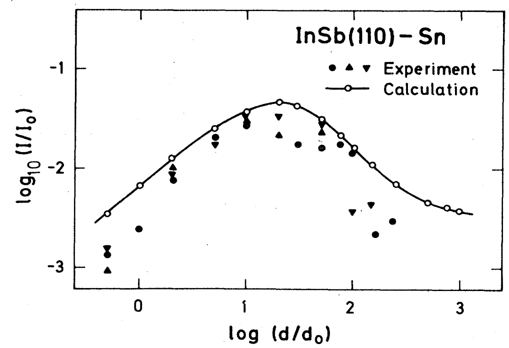

FIG. 2. Double-logarithmic plot of the loss intensity measured at a loss energy of 200 meV ($E_0=20$ eV, $\theta=80°$) for Sn layers on different samples (●,▲,▼) versus layer thickness. The intensity I is referred to that of the elastic peak I_0 and the thickness d to that of a Sn monolayer ($d_0\approx2$ Å). For comparison the calculated loss intensity at a loss energy of 15 meV is given in open circles (○).

beam, and poorly resolved shoulders near 10 and 23 meV. These two loss features and the corresponding gains at negative energies are due to the excitation of the coupled surface phonon-plasmon polaritons whose frequencies are determined by maxima of the surface loss function $-\text{Im}[1/(1+\epsilon)]$ of an IR-active semiconductor.[1,8,9] Furthermore, a broad structure with an onset near 200 meV is observed at an amplification factor of 1000.

Deposition of Sn causes a gradual suppression of these loss features. The broad structure at loss energies higher than 200 meV has disappeared at a Sn coverage of about two monolayers (ML), corresponding to approximately a layer thickness of 4 Å. The phonon-plasmon polariton losses are also lower in intensity; they cannot be resolved anymore at coverages around 10 ML. Simultaneously with increasing Sn coverage a monotonic background decreasing to higher loss energies develops. Its absolute value can easily be followed by comparing the measured loss signal at ~0.2 eV loss energy and the amplification factors in Fig. 1. The loss energy of 0.2 eV is convenient for this purpose since neither the phonon-plasmon losses nor the broad structure starting at ~0.2 eV contributes to the loss signal significantly. The background related to the Sn overlayers reaches its maximum intensity at coverages between 10 and 20 ML; in this range compared to the clean surface the loss intensity measured at 0.2 eV is higher by two orders of magnitude when referred to the intensity of the elastic beam. For coverages exceeding 20 ML the background decreases again in intensity. The overall behavior is shown in Fig. 2, where the loss signal measured at 0.2 eV is plotted in a double logarithmic plot versus the film thickness d. The intensity I is given relative to the value I_0 of the elastic peak and d is given in units of d_0, the thickness of 1 ML (~2 Å).

There is an additional effect, which is clearly seen in Fig. 1 for a Sn coverage of 75 ML. For coverages exceeding 30 ML a shoulder emerges at a loss energy of about 70 meV. At 75 ML it is best developed whereas it loses intensity again with further increasing Sn coverage. Above 150 ML it is not resolved anymore. Scanning electron micrographs with a spatial resolution of about 10 nm show that the surface of Sn layers of 50 ML thickness is essentially flat, but at 150 ML some roughness is found.

IV. DISCUSSION

In order to understand the effects, which are observed in HREELS on Sn layers being deposited on cleaved InSb(110) surfaces, it is necessary to have information about the morphological and structural nature of the deposit. The related questions have been investigated in detail by a number of experimental methods (electron and optical spectroscopies) in previous work.[4,5] It could be shown that on clean cleaved (110) surfaces at 300 K, Sn layers grow in an amorphous (or perhaps microcrystalline) α-Sn modification rather than as metallic β-Sn layers. Due to the chemical and structural similarity of semiconducting α-Sn with InSb the tetrahedral bonding order of the semiconducting Sn species is stable up to coverages of about 500 Å and up to temperatures of about 150 °C. On cleaved (110) surfaces which have been Ar bombarded and annealed as well as on Ar bombarded and on annealed InSb(100) surfaces even epitaxial growth of crystalline α-Sn has been observed.[5] Accordingly the Sn deposit which is studied in this work consists of semiconducting, noncrystalline α-type Sn layers which probably exhibit a vanishing band gap (as in bulk crystalline α-Sn). Up to coverages of about 150 ML, homogeneous layer-by-layer growth is found; only for thick layers (>150 ML) are roughening and surface inhomogeneities seen in scanning electron micrographs.

For the discussion of the spectral information obtained by HREELS we start with the clean cleaved InSb(110) surface (Fig. 1). The coupled surface plasmon-phononlike losses are observed as poorly resolved shoulders near 10 and 23 meV, respectively. According to a simple calculation within the framework of dielectric theory[10–12] this indicates a free-electron concentration of the doped crystals of 2×10^{16} cm^{-3}. This value for the carrier concentration is also obtained from IR-reflection measurements of the plasma edge on the InSb samples used. The broad shoulder with an onset near 200 meV extending to higher loss energies (Fig. 1) is due to the fundamental band-gap excitation of electron-hole pairs in InSb. From optical measurements the width of the bulk forbidden band is known to be 180 meV at 300 K.[13] This interpretation is consistent with the observed suppression of this structure after increasing Sn deposition (Fig. 1).

A theoretical model for the Sn layer effects must explain the loss shoulder near 70 meV which is best developed at about 75 ML and the monotonic background varying with Sn layer thickness. A qualitatively similar background has already been observed in HREELS by Backes and Ibach[6] for Ag layers on Si(111) and by Dubois *et al.*[7] for Ag on GaAs(110). In both cases an explanation based on the free-electron gas in the metal overlayers was adequate. Also in the present case the monotonic shape of the background and its dependence on Sn coverage suggest that it is due to free carriers in the Sn overlayer. In a simple model we therefore assume dielectric scattering on a layered medium consisting of a semi-infinite InSb substrate (dielectric function $\epsilon_{\rm InSb}$) with a Sn overlayer whose dielectric function $\epsilon_{\rm Sn}$ is essentially given by a Drude term

$$\epsilon_{\rm Sn}(\omega)=\epsilon(\infty)-\frac{\omega_p^2}{\omega(\omega+i/\tau)} . \tag{1}$$

The plasma frequency ω_p and the relaxation time τ, respectively, are related to the free-electron concentration n, the electronic effective mass m^* and the mobility μ by

$$(\hbar\omega_p)^2=\frac{\hbar^2e^2n}{\epsilon_0 m^*} , \tag{2}$$

$$1/\tau=e/m^*\mu . \tag{3}$$

The transport parameters m^* and μ as well as the free-carrier concentration n are not known for such an "amorphous" α-Sn film. In particular the mobility μ might deviate considerably from its bulk value in crystalline α-Sn.

In the following it is shown that the characteristic spectral shoulder observed between 10 and 70 meV loss energy, most strongly represented by coverages around 75 ML, allows the determination of the characteristic Sn parameters in Eqs. (1)–(3). Since no characteristic electronic transition energies are found in the known bulk band structure of α-Sn, an interpretation in terms of collective plasma excitations, rather than in terms of interband transitions, is suggested. The free-electron gas of the Sn layer exhibits interface plasmons both at the Sn/vacuum and at the Sn/InSb interfaces. In general these plasmons couple via their electric field thus giving rise to a characteristic dispersion.[10] For sufficiently thick Sn layers ($d \gg q_{\parallel}^{-1}$, d layer thickness, $q_{\parallel}$ wave vector transfer), however, these two modes do not couple and their frequency $\omega_{\rm sp}$ is simply given by

$$\epsilon_{\rm Sn}(\omega_{\rm sp})=-\epsilon_{\rm adj} , \tag{4}$$

where $\epsilon_{\rm adj}$ equals one for the vacuum interface and $\epsilon_{\rm InSb}$ for the opposite side. In the present experiment, where the wave vector transfer determined by the experimental conditions ranges in the order of $\frac{1}{350}$ Å^{-1}, coupling is expected to a certain extent at a Sn layer thickness of about 170 Å (=75 ML). Nevertheless Eq. (4) yields a rough first estimation for the characteristic Sn parameters contained in Eqs. (2) and (3). We assume that the loss shoulder at 75 ML is mainly determined by a loss near 70 meV and attribute this loss to the Sn/vacuum interface plasmon; neglecting any damping ($\tau\approx0$), Eqs. (1) and (4) yield [with $\epsilon_{\rm adj}=1$, $\epsilon(\infty)=24$,[14] and $\omega_{\rm sp}=70$ meV] a bulk plasmon energy $\hbar\omega_p$ for the Sn layer of 350 meV. This value can be used as a starting point for a numerical fit of calculated loss spectra to the experimental curve in Fig. 1 (75 ML). For the calculation of the loss spectra the inelastic-scattering cross section is obtained according to Ibach and Mills[15] by inserting into the surface loss function $-{\rm Im}(1+\tilde{\epsilon})^{-1}$ the effective dielectric function $\tilde{\epsilon}$ of the layer model

$$\tilde{\epsilon}=\epsilon_{\rm Sn}\frac{1+\Delta\exp(-2q_{\parallel}d)}{1-\Delta\exp(-2q_{\parallel}d)} , \tag{5}$$

with

$$\Delta=\frac{\epsilon_{\rm InSb}-\epsilon_{\rm Sn}}{\epsilon_{\rm InSb}+\epsilon_{\rm Sn}} .$$

For simplicity the dielectric function of the substrate $\epsilon_{\rm InSb}$ contains only the TO phonon oscillator contribution; free electrons are neglected since the carrier concentration is as low as 2×10^{16} cm^{-3} and the InSb surface plasmon frequencies lie close to the elastic peak. The Sn layer is described by Eq. (1). The loss spectra are calculated by integrating the differential inelastic-scattering cross section over the entrance aperture of the analyzer, simulating multiple energy gains and losses by a Poisson distribution and finally convoluting with the transmission function of the analyzer.[1] The energetic position of the losses is mainly controlled by the plasma frequency ω_p whereas the damping, i.e., the relaxation time τ mainly influences the band intensity. The best obtained fit to the experimental data is shown in broken line in Fig. 3. From this fit the bulk plasmon energy $\hbar\omega_p$ of the Sn layer is obtained as 377 meV and the damping constant $\hbar/\tau$ as 28 meV. As can be seen from the calculated curve ($\times3.3$) in Fig. 3 the shoulder consists of two broad losses, the one at 70 meV (derived directly from the experiment) and a second one at around 50 meV. This loss is identified as due to the Sn/InSb interface plasmon. Using Eq. (4), the dielectric function of InSb, and the determined parameters ω_p and $\hbar/\tau$ for the Sn overlayer, one obtains for this interface plasmon an approximate excitation energy of 52 meV. This value would, of course, only be correct if the two interface plasmons do not couple. The spectral shoulder is therefore due to the interface plasmons Sn/vacuum and Sn/InSb whose loss bands are not resolved because of strong damping. The plasmon at the Sn/InSb can be excited in the experiment since the decay length of its field amounts to about 350 Å ($=1/q_{\parallel}$) which exceeds the Sn

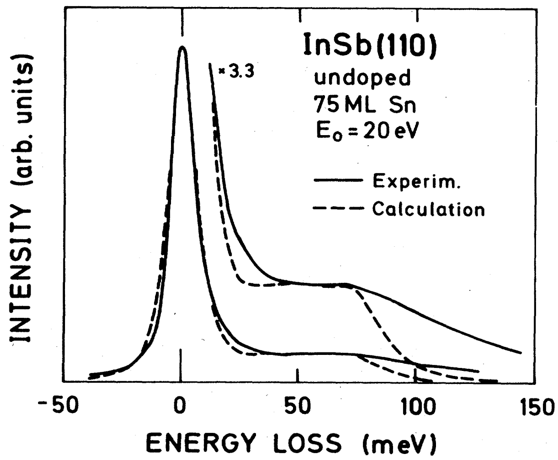

FIG. 3. Measured loss spectrum of a cleaved InSb(110) surface with a 75-ML thick Sn overlayer (solid curve, taken from Fig. 1). For comparison a calculated loss spectrum is plotted in broken line. For this calculation the Sn overlayer has been assumed to have a thickness of 170 Å and its dielectric response is modeled by a Drude "free-electron" dielectric function. The InSb substrate is assumed to be insulating.

layer thickness by a factor of 2.

The Sn plasmon energy $\hbar\omega_p$ determined to be ~ 377 meV and the damping constant $\hbar/\tau$ of about 28 meV allow further conclusions concerning the transport properties of this Sn layer. For a metallic β-Sn layer one would expect a plasmon energy higher than 10 eV. In accordance with previous work it is therefore concluded that the Sn layer is semiconducting. Equations (2) and (3) yield values for the electron concentration n and the mobility μ if the effective mass m^* were known. The conductivity of crystalline α-Sn arises from light electrons near the Γ point and heavy electrons in a band minimum near L being higher in energy by about 0.1 eV.[16] For higher carrier density the heavy electrons are important[14] and their effective mass m^* of 0.13 m_0 is therefore used as an approximate value in Eqs. (2) and (3). One then obtains for the electron density n in the "amorphous" α-Sn film a value of 1.3×10^{19} cm^{-3} and the mobility μ follows as 318 cm^2/V s. The obtained electron density is consistent with data, which have been obtained on crystalline α-Sn.[14] The mobility is significantly smaller than literature values, which are reported to be between 1×10^3 and 3×10^3 cm^2/V s for heavy electrons in crystalline α-Sn. This deviation is, of course, expected for thin layers which are furthermore amorphous or polycrystalline. In such layers the mobility is decreased by surface scattering and scattering on all kinds of defects.

After the properties of the Sn overlayers have been determined in the present model, the characteristic background behavior (Fig. 2) can be considered further. Figure 4 shows for several Sn film thicknesses inelastic scattering cross sections which have been calculated by using the layer model [Eq. (5)] and Sn parameters determined from the fit in Fig. 3. Multiple energy losses and broadening of the loss structures due to the spectrometer transmission function are not taken into account. The sharp structure at 24 meV is due to the surface phonon of

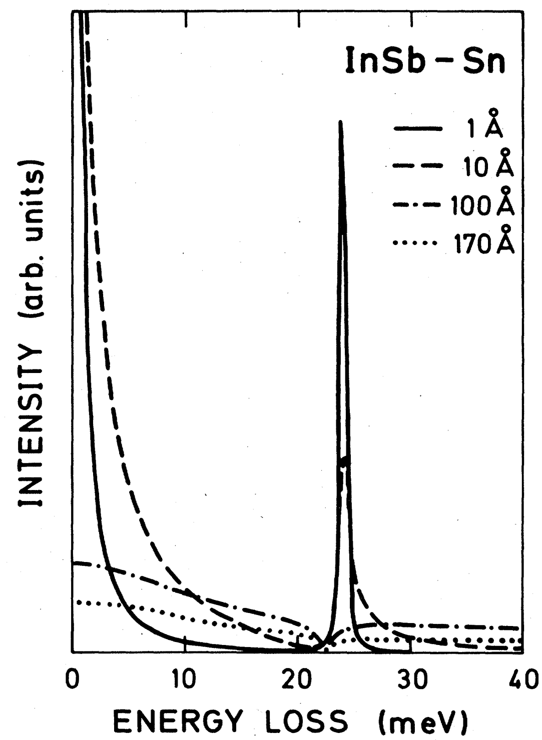

FIG. 4. Calculated inelastic-scattering cross sections for dielectric scattering on a layer model (insulating InSb substrate, Sn overlayers described by the Drude "free-electron" dielectric function). Various Sn layer thicknesses have been assumed ($E_0=20$ eV, specular reflection scattering geometry $\theta=80°$). Multiple scattering, elastic peak, and spectrometer broadening are not taken into account.

the InSb substrate assumed as insulating (no free electrons). The emergence of a monotonic background with increasing film thickness is clearly seen. It reaches its maximum intensity (e.g., at 15 meV) near a film thickness of about 28 Å and then decreases again. In the calculated spectra the InSb phonon becomes suppressed at 10 Å and at 100 Å it is only seen as a slight dip in the curves. The monotonic background resulting from the calculations exhibits the behavior of the experimental data. For a comparison we assume that its dependence on thickness is similar at different loss energies. It is then possible to make the comparison at loss energies where a minimum contribution from other excitations (phonons, band-gap structure) is expected. In Fig. 2 therefore, the measured background at 200 meV is compared with the inelastic scattering cross section (from Fig. 4) at 15 meV. Good agreement is found both with respect to the general shape and to the location of the maximum of the curve (~ 20 ML, which approximately corresponds to 40 Å). For low coverages an almost linear increase with film thickness d follows as is expected from dipole theory for scattering on a thin overlayer.[12] For thicker metallic layers Backes and Ibach[6] derive a d^{-1} decrease with increasing thickness. This dependence is also approximately found for film thicknesses that exceed that which corresponds to the maximum in Fig. 2.

The increase and subsequent decrease of the background loss signal with increasing Sn layer thickness can be understood qualitatively in terms of inelastic scattering on the possible collective modes of the Sn layer on top of the InSb substrate. The two frequencies of the interface modes (with dispersion) are obtained from the poles of the surface loss function of a layered medium [see Eq. (5)]. This condition yields

$$\frac{\epsilon_{\rm Sn}(\omega)+1}{\epsilon_{\rm Sn}(\omega)-1}\,\frac{\epsilon_{\rm Sn}(\omega)+\epsilon_{\rm InSb}}{\epsilon_{\rm Sn}(\omega)-\epsilon_{\rm InSb}}=e^{-2q_{\|}d} . \tag{6}$$

For each $q_{\|}d$ value Eq. (6) has two solutions, the dispersion branches for the two interface modes. When $\epsilon_{\rm Sn}$ is simply a Drude dielectric function as in the present assumption, the solutions show the following behavior. For large $q_{\|}d$ ($\rightarrow\infty$) the branches correspond to the uncoupled modes of the Sn/InSb ($\epsilon_{\rm Sn}=-\epsilon_{\rm InSb}$) and of the Sn/vacuum interface ($\epsilon_{\rm Sn}=-1$). For small $q_{\|}d$ ($\rightarrow 0$) values the upper branch approaches the longitudinal bulk plasmon frequency ω_p of the Sn layer [$\epsilon_{\rm Sn}(\omega_p)=0$]. Even though it belongs to a pole in the surface loss function, this excitation mode expected at 377 meV does not give any significant structure whether in the calculated scattering cross section or in the measured spectra (Fig. 1). Important for the present considerations is the lower branch which exhibits for small $q_{\|}d$ values a dispersion as follows:

$$\omega^2(q_{\|})=\frac{\omega_p^2 q_{\|}d}{1+\epsilon_{\rm InSb}} . \tag{7}$$

For an explanation of the background one has to keep in mind that the analyzer accepts wave vector transfers up to an upper limit q_c only. Accordingly for small thickness d of the Sn layer the detectable $q_{\|}d$ values lie below $q_c d$, i.e., the observed losses are restricted to energies $\hbar\omega<\hbar\omega(q_c d)$ according to Eq. (7). Growing thickness d allows higher loss energies [Eq. (7)] and more and more modes of the lower dispersion branch are excited thus contributing to the extending and increasing monotonic background. For even thicker layers the possible $q_{\|}d$ reach that region of the dispersion curves where the uncoupled interface modes can be excited, the shoulder due to their excitation becomes prominent in the spectra and the background decreases again.

A further interesting observation is the suppression of the InSb surface-phonon-like loss at about 23 meV for Sn layer thicknesses of about 20 Å which are far below the decay length ($\sim$200 Å) of the electric field of the phonon. A similar phenomenon has also been observed by Dubois *et al.*[7] for Ag layers on GaAs. They explain the effect in terms of an interaction of the surface phonon mode with the low-energy plasmon modes of the metallic overlayer. With increasing film thickness d the layer plasmon mode frequency approaches the frequency of the InSb substrate surface phonon. According to Dubois *et al.*[7] this situation leads to a suppression of the substrate surface phonon mode. A similar estimation for the present system leads to a critical Sn film thickness of about 7 Å, where the InSb surface phonon should disappear. This is in good agreement with the experimental data.

V. CONCLUSION

The present study is interesting in several respects. It demonstrates again that dielectric theory can be applied to the description of inelastic-electron scattering on conducting overlayers on semiconductors. With respect to the particular system Sn/InSb(110) the present results support the recently obtained information that the Sn layers—at least for lower coverages—grow as amorphous or polycrystalline semiconducting α-Sn on cleaved InSb(110).

It is shown that HREELS, if applied to the study of such overlayer systems (metallic or semimetallic) on semiconductors, can yield information about electrical transport parameters in the overlayer and in connection with this maybe also about morphological properties. The technique might in the future be interesting also with respect to studies of epitaxially grown heterostructures.

ACKNOWLEDGMENT

This work was financially supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) within the Sonderforschungsbereich 202 (Aachen).

[1]R. Matz and H. Lüth, Phys. Rev. Lett. **46**, 500 (1981).
[2]A. Ritz and H. Lüth, Phys. Rev. Lett. **52**, 1242 (1984).
[3]A. Ritz and H. Lüth, J. Vac. Sci. Technol. (to be published).
[4]M. Mattern and H. Lüth, Surf. Sci. **126**, 502 (1983).
[5]R. F. C. Farrow, D. S. Robertson, G. M. Williams, A. G. Cullis, G. R. Jones, I. M. Young, and P. N. J. Dennis, J. Cryst. Growth **54**, 507 (1981).
[6]U. Backes and H. Ibach, Solid State Commun. **48**, 445 (1983).
[7]L. H. Dubois, G. P. Schwartz, R. E. Camley, and D. L. Mills, Phys. Rev. B **29**, 3208 (1984).
[8]H. Ibach, Phys. Rev. Lett. **24**, 1416 (1970).
[9]E. A. Stern and R. A. Ferrell, Phys. Rev. **120**, 130 (1960).
[10]H. Raether, in *Springer Tracts in Modern Physics,* edited by G. Hohler (Springer, Berlin, 1965), Vol. 38, p. 84ff.
[11]J. Geiger, *Elektronen und Festkörper* (Vieweg, Braunschweig, 1968).
[12]H. Lüth, Surf. Sci. **126**, 126 (1983).
[13]S. Zwerdling, B. Lax, and L. M. Roth, Phys. Rev. **108**, 1402 (1957).
[14]O. Madelung, in *Semiconductors,* Vol. III/17a of *Landolt-Börnstein New Series* (Springer, Berlin, 1982), p. 127ff.
[15]H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).
[16]S. Groves and W. Paul, Phys. Rev. Lett. **11**, 194 (1963).