surface with respect to vibrations in the z direction, and "single-layer" modes are obtained in which the first layer, the second layer, etc. vibrate almost independently. Similarly, at the point $\bar{X}$ (center of the zone edge) there are "single-layer" modes for in-plane vibrations.

[4]This behavior appears to be related to a result concerning Rayleigh waves in anisotropic elastic media which was obtained by D. C. Gazis, R. Herman, and R. F. Wallis [Phys. Rev. 119, 533 (1960)]. These authors found that for the (100) surface of a cubic crystal, and for certain values of the elastic constants, there is a range of excluded directions of propagation about the [110] direction, but that this direction itself is not excluded.

[5]Yu. V. Gulyaev, Zh. Eksperim. i Teor. Fiz.—Pis'ma Redakt. 9, 63 (1969) [JETP Letters 9, 37 (1969)]; J. L. Bleustein, Appl. Phys. Letters 13, 412 (1969).

OBSERVATION OF SURFACE BOUND STATE AND TWO-DIMENSIONAL ENERGY BAND BY ELECTRON TUNNELING

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Using electron tunneling, we have made direct observation of a surface bound state of electrons localized in a narrow accumulation layer at the InAs-oxide interface. The Landau-level structure of the two-dimensional energy band, associated with the bound state, has been studied in a magnetic field up to 85 kG.

In narrow accumulation or inversion layers at semiconductor surfaces, quantization of electronic motion normal to the surface leads to discrete bound-state energy levels binding electrons to the surface.[1] Corresponding to each surface bound state, there is a band of two-dimensional conduction states, due to a continuum of the electronic motion parallel to the surface, with its band edge at the surface-state binding energy. These states have been referred to as space-charge–induced localized states[2] and also as electric sub-bands.[3] Previously, only experiments on surface transport properties have yielded evidence for their existence.[4] It is the purpose of this Letter to report the first direct observation of these surface bound states and to demonstrate that electron tunneling offers a simple and yet powerful tool for studying the electronic energy structure of these states.

The measurements were made on n-type degenerate InAs-oxide-Pb tunnel junctions using standard techniques.[5] The fabrication procedure for these tunnel junctions has been discussed previously.[6] At present, little is known about the oxide layer, which was thermally grown on the surface of single-crystal InAs. We used Pb films as counterelectrodes so that the tunneling characteristics of superconducting Pb could be used as proof that electron tunneling was the current-carrying mechanism through the junction.[5] The results discussed in this Letter have not been observed in junctions which did not show this proof of tunneling.

We have deduced from tunneling measurements that a narrow accumulation layer of electrons, which may result from positively charged immobile centers in the oxide, exists at the InAs-oxide interface.[7] The two-dimensional energy band corresponding to each surface bound state of the electrons in this accumulation layer may be approximated by[1] $E(k_{\|}) = \hbar^2 k_{\|}^2/2m_{\|}^* + E_b$, where E_b is the surface-state binding energy, $k_{\|}$ is the wave vector parallel to the surface, and $m_{\|}^*$ is the effective mass parallel to the surface. Both E_b and $m_{\|}^*$ have been determined directly from the tunneling results. E_b is determined from the bias at which the two-dimensional band edge is observed in the junction conductance (dI/dV). When a magnetic field is applied normal to the surface, the dI/dV-V curves of the junction exhibit oscillations which reflect the Landau levels of the two-dimensional energy band.[6,8] The period of the oscillations, which equals the Landau-level separation, determines the value of $m_{\|}^*$.

Figure 1 shows the conductance-versus-bias curve of an n-type degenerate ($n = 5.5\times10^{17}/\mathrm{cm}^3$) InAs-oxide-Pb tunnel junction at 4.2°K when the Pb superconductivity is quenched by applying a magnetic field. At a bias equal to the longitudinal optical (LO) phonon energy ($V \approx 30$ mV) of InAs,[9] a decrease in conductance (~2%) is observed in both bias directions. This structure must result from the electron LO-phonon interaction in the InAs electrode. However, the structure is in contrast to the phonon-assisted

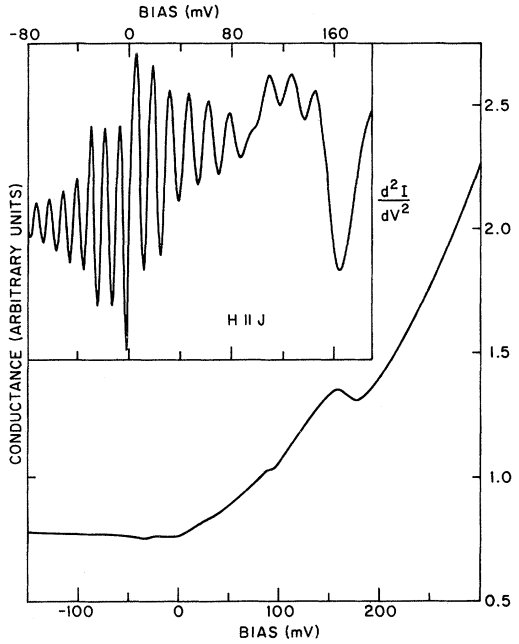

FIG. 1. The conductance-versus-bias curve of an n-type InAs-oxide-Pb (normal state) tunnel junction at 4.2°K. The InAs is degenerate, having bulk electron concentration $n \approx 5.5 \times 10^{17}/\text{cm}^3$. The bias sign refers to that of the Pb electrode. The insert shows the d^2I/dV^2 versus bias curve when a magnetic field (35 kG) is applied normal to the junction surface.

tunneling structure, which consists of an increase in conductance at the phonon energy in both biases.[10] It also differs from the asymmetric structure which has been attributed to electronic self-energy effect due to electron interactions with optical phonons in semiconductors.[11] As far as we know, structure of this symmetry has not been observed previously but has been discussed by Appelbaum and Brinkman.[12] We will discuss it in more detail in a future article.

Two additional structures have been observed in the Pb positive bias. At $V = +95$ mV, the conductance decreases by about 4%. This decrease results from the cutoff of the bulk electron density of states at the bottom of the conduction band of bulk InAs. The bias, $V = 95$ mV, measures the Fermi degeneracy of the bulk InAs sample.[13] The Fermi degeneracy deduced from the parabolic-band approximation using $m^*/m_0 = 0.027$ [6,7] is $\epsilon_F = 100$ meV, which is in good agreement with the tunneling result.

At higher biases, the Fermi level in Pb is aligned with the energy gap of bulk InAs. The number of electrons of the bulk sample that can tunnel into the Pb electrode remains constant. The observed increase in conductance with increasing bias is due to bias effects on the barrier potential and the two-dimensional energy band of the surface bound states, which extends into the bulk InAs energy gap.

The conductance curve, as shown in Fig. 1, starts to decrease at $V \approx 158$ mV and reaches a local minimum at $V \approx 178$ mV. This structure is a decrease in conductance similar to the structure due to the bulk InAs conduction band edge observed at $V \approx 95$ mV. We interpret it as due to the cutoff of the electron density of states at the two-dimensional energy-band edge of the surface bound state.[14] As seen in Fig. 1, this surface effect is much stronger than the bulk effect. We take the bias $V = 168$ mV, at which the minimum in second derivative d^2I/dV^2 corresponding to the steepest conductance decrease is observed, as the binding energy of the surface bound state measured from the Fermi level.

Further evidence that the conductance structure at $V \approx 168$ mV reflects the two-dimensional energy-band edge of the surface bound state is seen in the Landau-level structure observed in the tunneling characteristics of the tunnel junction. When a magnetic field is applied normal to the junction surface (i.e., parallel to the tunnel current), two sets of oscillations have been observed in the dI/dV-V and d^2I/dV^2-V curves. The insert of Fig. 1 shows a d^2I/dV^2-V curve of the tunnel junction when a magnetic field of 35 kG is applied normal to the surface. It is apparent that there are two sets of oscillations. The set which starts from bias equal to the bulk conduction band edge reflects the Landau levels of the conduction band of bulk InAs. The other set, which starts from bias equal to the two-dimensional band edge, reflects the Landau levels of the two-dimensional energy band of the surface bound state. When the magnetic field is applied parallel to the junction surface, only the set of oscillations which reflects the Landau levels of the conduction band of bulk InAs is observed.[6,8] The two-dimensional surface states cannot sustain Landau orbits when the magnetic field is parallel to the surface.

The oscillatory conductance data pertinent to the Landau-level structure of the two-dimensional energy band of the surface bound state are shown in Fig. 2. At a given magnetic field, which is applied normal to the junction surface, oscillations are observed in the dI/dV-V and d^2I/dV^2-V curves. The bias positions of the d^2I/dV^2 minima which correspond to the steepest decrease of conductance in the Pb positive bias are plotted as a function of the magnetic field. The resulting

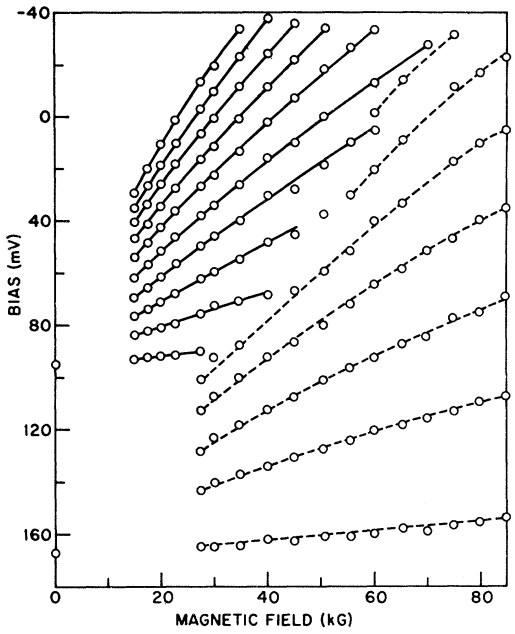

FIG. 2. Landau levels of the two-dimensional conducting states at the InAs-oxide interface and Landau levels of the conduction band of bulk InAs. The data points are explained in the text. The solid curves and the dashed curves are drawn through the data points to show that the data points form two distinct sets of levels. The bias measures the electron energy with respect to the Fermi level ($\epsilon_F \approx 95$ meV). The bias sign refers to that of the Pb electrode.

Landau levels group themselves into two distinct sets. In the zero-field limit, one set converges onto the conduction-band edge of bulk InAs and the other set converges onto the binding energy of the surface bound state. Thus, it is evident that the electronic states of the accumulation layer form a two-dimensional energy band with its band edge at the surface-bound-state binding energy. As seen from the Landau-level structure shown in Fig. 2, the two-dimensional energy band is also nonparabolic. Its effective mass is approximately equal to the bulk conduction-band mass.

The electron potential well of the surface accumulation layer may be approximated by $V(z) = -V_0 \exp(-z/\lambda)$ and $V(0) = \infty$, where λ is the electron screening length in InAs and z is the distance from the InAs-oxide interface into the bulk InAs sample. The depth V_0 of the potential well can be estimated from the binding energy of the bound state.[2] For the junction discussed above, no other conductance structure has been observed with bias up to $V = +400$ mV. We may, therefore, assume that there is only one bound state inside the potential well. If we use 0.02 for the effective mass normal to the surface and 15 for the dielectric constant,[9] the estimated potential well parameters are $\lambda \approx 30$ Å and $V_0 \approx 0.8$ eV.

Finally, the number of bound states in the potential well may be varied by varying the Fermi degeneracy of the bulk InAs. By decreasing the carrier concentration, we expect to increase λ and thus to increase the number of bound states. This has in fact been observed. Using samples with a bulk carrier concentration $n = 2.2 \times 10^{16}/\text{cm}^3$, we have observed two surface bound states. Their binding energies are $E_b = 35$ and 153 meV (measured from the bulk conduction-band edge). The estimated potential-well parameters are $\lambda \approx 50$ Å and $V_0 \approx 0.8$ eV. The oscillatory tunneling characteristics, which reflect the Landau levels of both of the two-dimensional energy bands associated with the two bound states, have also been observed when the magnetic field is applied normal to the junction surface.

I would like to thank D. E. Aspnes, W. L. McMillan, J. C. Phillips, and J. M. Rowell for valuable conversations, and L. N. Dunkleberger for technical assistance.

[1]J. R. Schrieffer, in Semiconductor Surface Physics, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, Penn., 1957), p. 55.

[2]See, for example, C. B. Duke, Phys. Rev. 159, 632 (1967); and D. J. BenDaniel and C. B. Duke, Phys. Rev. 160, 679 (1967).

[3]F. Stern and W. E. Howard, Phys. Rev. 163, 816 (1967).

[4]See, for example, P. Handler and S. Eisenhouer, Surface Sci. 2, 64 (1964); A. B. Fowler, F. F. Fang, W. E. Howard, and P. J. Stiles, Phys. Rev. Letters 16, 901 (1966); and S. Kawaji and H. C. Gatos, Surface Sci. 7, 215 (1967).

[5]See, for example, W. L. McMillan and J. M. Rowell, in Superconductivity, edited by R. D. Parks (Marcel Dekker, New York, 1969), Chap. 11.

[6]D. C. Tsui, to be published.

[7]It has been known for many years that a degenerate n-type layer exists on p-type bulk InAs. See, for example, O. Madelung, Physics of III-V Compounds (Wiley, New York, 1964), Chap. 4.

[8]D. C. Tsui, to be published.

[9]E. Burstein, in Phonons and Phonon Interactions, edited by T. A. Bak (Benjamin, New York, 1964), p. 276.

[10]See, for example, A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. 125, 877 (1962).

[11]See, for example, L. C. Davis and C. B. Duke, Phys. Rev. 184, 764 (1969).

[12]J. A. Appelbaum and W. F. Brinkman, to be pub-

lished.

[13]In metal-oxide-semiconductor junctions, band edges of the bulk semiconductor have previously been observed. See, for example, P. V. Gray, Phys. Rev. 140, A179 (1965); and L. Esaki and P. J. Stiles, Phys. Rev. Letters 16, 1108 (1966).

[14]BenDaniel and Duke (Ref. 2) have calculated the conductance due to two-dimensional energy bands of surface bound states for Al-oxide-Bi junctions. At band edges, their results show abrupt conductance decrease and are in good agreement with our observation. We have not observed any conductance structure which may be attributed to Van Hove singularities in the density of states of the two-dimensional energy band.

ENERGY BAND STRUCTURE OF COPPER BY THE EMPIRICAL PSEUDOPOTENTIAL METHOD*

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The electronic band structure of copper is calculated using the empirical pseudopotential method. A nonlocal d-wave potential with a damping factor is used to provide the potential for the d electron. The results agree well with the available experimental data and with theoretical band calculations using other methods. It is anticipated that the empirical pseudopotential method can be used for other noble metals and even extended to noble metal compounds, transition metals, and transition metal compounds.

Pseudopotentials obtained from experimental data have been extremely valuable in yielding information about the electronic structure of solids.[1] Fermi surface data have been used for metals, and optical properties have yielded a vast amount of information about the potentials appropriate to semiconductors and insulators.[1,2] This later method has been called the empirical pseudopotential method (EPM) and very accurate band-structure calculations have resulted[3] from its application. It has even been possible to associate the pseudopotentials with the atoms in a semiconductor compound and to use these potentials in different crystal structures or different compounds.[4] It was this possibility which motivated the present work. An EPM scheme for the noble metals could allow band calculations of noble metal compounds. We also anticipate that the present work could result in an EPM for transitions metals and would allow calculations of transition metal compounds which are currently the objects of intensive study.

Because of the strong s-d interaction[5] between the $(4s)^1$ and $(3d)^{10}$ electrons, and the fact that the $(3d)^{10}$ electrons experience a strong core potential, a local pseudopotential calculation is not possible. This is what has motivated some authors to try new schemes, and some very successful analyses of the electronic properties of Cu[6] have been done based on schemes[7] which involve the mixing of the tight-binding method for the d bands and a pseudopotential-like method for the s and p bands. We have been able to treat the d bands without resorting to the tight-binding method by using an $l=2$ nonlocal potential. This method was also used by Lee and Falicov[8] for potassium and by Fong and Cohen[9] for KCl.

The experimental information required for our calculations are given by Spicer,[10] Gerhardt,[11] and Fadley and Shirley.[12] Spicer used photoemission data to derive the width of the d bands and the gap of the p band at $L(L_2')$ to the Fermi level. The values for these gaps are 2.8 and 0.35 eV, respectively. Gerhardt measured the piezoreflectance of Cu for different crystal orientations. He obtained energy gaps between the filled d bands and the vacant p band at X as well as the gaps between the filled p band and the vacant s band at L. The values he obtained are $E(X_5 \rightarrow X_4')$ = 4.0 eV and $E(L_2' \rightarrow L_1^u)$ = 4.5 eV, where u refers to the upper L_1 band. Fadley and Shirley determined the width of the d bands to be 3.0 eV by x-ray spectroscopy. We will compare these values with the theoretical values after we describe the theoretical calculation.

The crystal structure of copper is fcc with lattice constant $a = 3.61$ Å.[13] There is one atom per unit cell; we set the origin of the coordinate sys-