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Direct Photoelectric Measurement of the Interface-State Density at a Pt-Si Interface

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From infrared photoelectric measurements, we have obtained a density of the interface states lying between 0.745 and 0.825 eV from the silicon conduction band at a Pt-Si interface. We show the following: The transitions occur preponderantly from a level ~0.3 eV below the platinum Fermi level; a peak exists in the interface-state density at 0.79 eV from the silicon conduction band; and the pseudo Fermi level in the semiconductor moves up with forward bias.

In this communication we present the first direct experimental evidence, to our knowledge, of the existence of interfacial states in the band gap of silicon by photoemission. Some of these interfacial states were qualitatively predicted by Heine[1] on the basis of electron-wave-function matching at either side of a metal-semiconductor interface. The existence of interface states was first demonstrated by Bardeen[2] from interface pinning of the Fermi level for metals of different work function, and then the location of a peak in the interface-state density of a Au-Si diode was estimated by Crowell and Roberts[3] from capacitive measurements. For our investigation, we have used a Pt-Si interface so as to photoinject electrons from platinum to silicon. A spectral analysis of the photocurrent I as a function of $h\nu$ for low-energy photons (<0.8 eV) reveals the existence of interface states in the band gap of semiconductor.

Slices of Si (111) (n type, 10 Ω cm) were mechanically and chemically polished, then rinsed in hydrofluoric acid before platinum evaporation in ultrahigh vacuum (<10^{-9} Torr). The Ohmic contacts were made with gallium, and the ensemble showed the usual Schottky diode caracteristic of current and capacitance as a function of voltage. In the same mechanical assembly we obtained the photoemission using a modified Beckman DK 2A spectrophotometer with a tungsten-lamp source, that was calibrated with a Schwartz thermopile. The incident light traversed the silicon before hitting the silicon-platinum interface. The photocurrent measurement was done at 400 Hz by synchronous detection with a low-impedance preamplifier, while a continuous bias voltage was maintained by a battery.

From the photoelectric yield of electrons per photon as a function of $h\nu$, as well as measurement of capacitance in reverse bias, we determine the potential barrier $\psi_B = 0.91 \pm 0.05$ eV, in agreement with values already published in the literature.[4] At lower photon energy, we observe a supplementary electron excitation, of the order of 10^{-11} to 10^{-13} A. The mode of detection rules out any spurious effects arising from the geometry or polarization. The disappearance of the photocurrent in the absence of illumination while the mechanical chopper is on, rules out the existence of induction currents or any vibration-modulated currents. This excitation, we shall argue below, can be unambiguously attributed to interface states. If one normalizes the photoelectric yield curve (forward bias decreasing the interface electric field gives a lower collection efficiency) and plots it as a function of $h\nu$, one obtains a typical normalized yield, $Y(h\nu, V)$, shown in Fig. 1 (at 300°K). The beginning (not

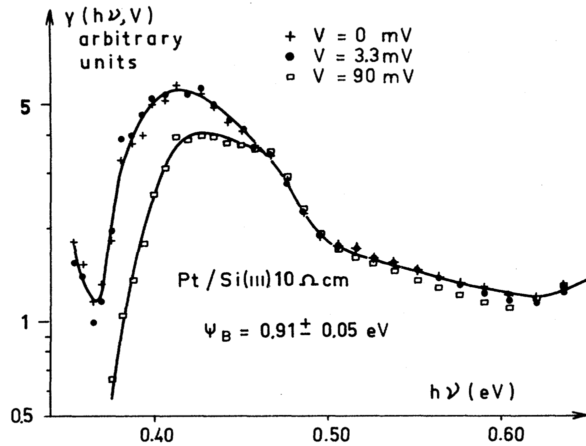

FIG. 1. Normalized photoelectric yield $Y(h\nu, V)$ versus photon energy $h\nu$ for a given forward bias V.

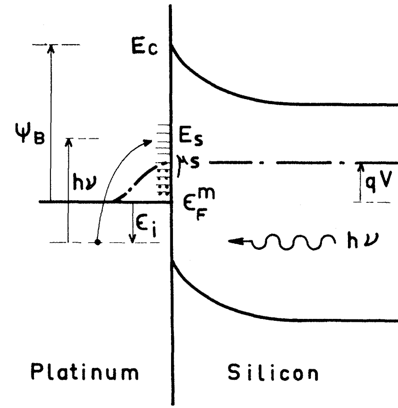

FIG. 2. Schematic energy-band diagram with an applied forward bias for a Pt-Si interface.

given here) of the high photoelectric yield above 0.9 eV represents the emission from states below the Pt Fermi level to the bottom of the conduction band. The interpolation $\sqrt{Y}=f(h\nu)$ gives the barrier heights[5] ψ_B we have talked about. The broad peak observed in photocurrent below 0.5 eV represents emission from the metal into the unoccupied interface states on the silicon. Figure 1 also shows that the photoelectric yield associated with the peak diminishes with applied forward bias.

In order to extract some quantitative information from this data, we have used the following simple analysis based on two assumptions: (a) The pseudo Fermi level μ_s at the semiconductor interface sweeps upward by an amount qV towards the conduction band as one applies a forward bias V. (b) The photoelectrons come from an unique energy level ϵ_i in the metal, not necessarily the Fermi level of the metal, $\epsilon_F{}^m$ (taken here as energy origin). The relevant energy levels are explained in Fig. 2.

The photoelectric yield Y is given, in the case of indirect transitions,[6] by

$$Y(h\nu)=A\int n_m(\epsilon)n_s(\epsilon+h\nu)|M_m s|^2 S(\epsilon,h\nu)\,d_\epsilon,$$

where $n_m(\epsilon)$ is the density of occupied states in the metal and $n_s(\epsilon)$ is the density of *unoccupied* surface states at the interface. Both the transition matrix element $|M_m s|^2$, as well as the shape function $S(\epsilon, h\nu)$, are often, as here, assumed constant. By using assumption (b), $n_m(\epsilon)=N_m\delta(\epsilon-\epsilon_i)$, we obtain the simplified expression

$$Y(h\nu, V)=KN_m(\epsilon_i)n_s(\epsilon_i+h\nu). \qquad (1)$$

If our assumption (a) is correct, the density of unoccupied surface states will be given by

$$n_s(\epsilon_i+h\nu)=N_s\left\{1+\exp\left[\frac{qV-(\epsilon_i+h\nu)}{kT}\right]\right\}^{-1}, \qquad (2)$$

where N_s is the total number of interface states. This permits us to write the ratio of normalized photoelectric yield, with and without the applied forward voltage V, as

$$\frac{Y(h\nu,0)}{Y(h\nu,V)}=\left\{1+\exp\left[\frac{qV-(\epsilon_i+h\nu)}{kT}\right]\right\}\times\left\{1+\exp\left[-\frac{\epsilon_i+h\nu}{kT}\right]\right\}^{-1}. \qquad (3)$$

For $\epsilon_i+h\nu>2kT$, the denominator of Eq. (3) approaches unity; one obtains

$$R(h\nu,V)=\frac{Y(h\nu,0)}{Y(h\nu,V)}-1=\exp\left[\frac{qV-(\epsilon_i+h\nu)}{kT}\right]. \qquad (4)$$

The experimental points obtained from $V=0$ and $V=90$ mV fall completely, in a semilogarithmic plot, on the theoretical straight line in Fig. 3. No adjustable parameters are needed. For the value $R(h\nu, V)=1$, (4) gives us the relation $\epsilon_i+h\nu=qV$, and thus from the knowledge of the corresponding experimental $h\nu$ and qV, ϵ_i can be deduced. We find that electrons are for the most part emitted from 0.3 eV below the Fermi level of the platinum in the photon energy range $0.376<h\nu<0.456$. A final verification of Eq. (4) comes from the slope of Fig. 3, which equals $1/kT$, and corresponds exactly to $kT=26$ meV, i.e., room temperature, as it should.

Thus, from our data, both assumptions (a) and (b) are completely vindicated and have also been corroborated by applied voltages other than the

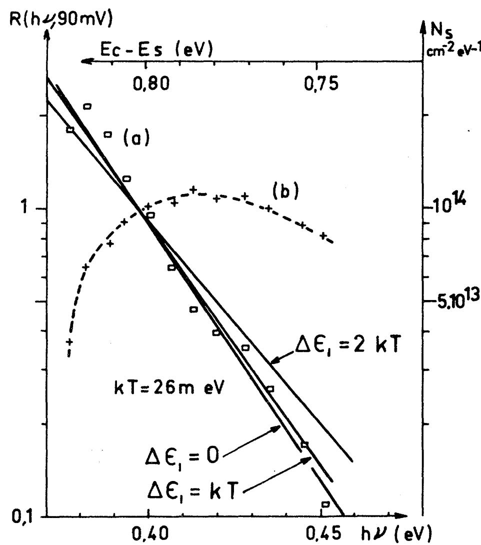

FIG. 3. (a) $R(h\nu,\ 90\ \text{mV}) = Y(h\nu, 0)/Y(h\nu,\ 90\ \text{mV}) - 1$. $T = 300°\text{K}$; $kT = 26$ meV. Open squares, experimental points. Solid lines, theoretical lines $\Delta\epsilon_i = 0$, $\Delta\epsilon_i = kT$, $\Delta\epsilon_i = 2kT$, for a rectangular distribution of initial states $(\epsilon_i - \Delta\epsilon_i, \epsilon_i + \Delta\epsilon_i)$. (b) Density of interface states versus energy from Fig. 1.

ones shown here.

In photoemission from bulk platinum,[7] strong transitions are observed, attributed to a peak in the distribution of initial states around 0.2 ± 0.15 eV below the Fermi level. Results of rectangular distributions of initial states $(\epsilon_i - \Delta\epsilon_i, \epsilon_i + \Delta\epsilon_i)$ are shown in Fig. 3, with $\epsilon_i = kT$ and $2kT$, at 300°K. It is seen that for $\epsilon_i = 2kT$ the agreement with the data starts getting poor. It is well known that the density of states gets relatively broadened in bulk photoemission experiments.[8] The sharp distribution (~0.05 eV) that fits the data agrees with the fine structure calculated theoretically.[9]

As to the density of interface states shown in Fig. 3, we note that the photoemission experiment does not give an absolute magnitude of N_s. We can deduce N_s by measuring differential junction capacitance and conductance in forward bias as a function of frequency because, in this case, occupation of surface states varies with bias. This procedure is analogous to that used by Nicollian and Goetzberger.[10] We were able to overcome the difficulty[11] arising in forward bias from series resistance. We could obtain, from the measured parallel capacitance and conductance, relevant values for differential interface capacitance and conductance. For the mechanics of obtaining N_s from these, the reader may consult Ref. 10 cited above. The density reported in Fig. 3 is at best an order-of-magnitude estimate.

The mechanism of current generation from disequilibrium in the occupation of interface states is similar to that observed in conductance studies of surface states in metal-oxide-semiconductor structures and has been studied in detail by Nicollian and Goetzberger.[10] The basic principles are derived from the work of Shockley and Read.[12] In the dark, we have thermal equilibrium between the metal, surface states, and conduction band; i.e., from the principle of detailed balance, thermal generation is equal to recombination for surface states and the conduction band. The external low-impendance circuit prevents all additional variation of voltage, i.e., of the quasi Fermi level, so that the excess of thermal generation originating from excess concentration of electrons in surface states due to illumination cannot be compensated for by excess recombination (as should be the case in an open circuit where it should have a new quasi Fermi level). This results in the photogenerated disequilibrium current that we measure. Such a behavior is supported experimentally by the observation of a constant phase (the same physical mechanism) in the photocurrent from high- ($h\nu > \psi_B$) to low-photon energy.

In conclusion, we find the following:

(1) Photoelectrons are provided from states in the platinum 0.3 eV below its Fermi level, in agreement with photoemission spectroscopy[7] and x-ray photoelectron spectroscopy.[13]

(2) The pseudo Fermi level at the interface can be made to sweep upward by an applied forward voltage. A similar result was implicitly demonstrated theoretically by Gossick[14] and was postulated explicitly by Roberts and Crowell.[15] This provides an elegant means to vary the occupation of interface states.

(3) The density of interface states shows a maximum at 0.125 eV above the platinum Fermi level, or 0.79 ± 0.05 eV from the bottom of the silicon conduction band. If we suppose, in regard to the weak variation of ψ_B with metal,[1] a similar weak variation of surface states with metal, this is in agreement with the estimated distance, 0.83 eV, for the surface-state peak density from the conduction band derived by Crowell and Roberts[3] for Au-Si.

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Theory of the Vibrations of Dilute Quantum Crystal Alloys*

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We present a theory for the lattice dynamics of dilute impure quantum crystals which is quantum mechanically exact within the self-consistent phonon approximation. The theory predicts that mass-defect–induced changes in properties depending linearly on the scattering amplitude (e.g., specific heat) are largely canceled by a self-consistent force-constant renormalization. Changes depending on even powers of the scattering amplitude (e.g., thermal resistivity) are enhanced by the quantum-crystal effects.

The calculation of the vibrational properties of a harmonic crystal with a defect atom is one of the few exactly solvable quantum-mechanical problems and has received considerable attention.[1] Typically, the mass of the defect atom is different from that of the host atoms, and the harmonic force constants coupling the defect to its neighbors are different from those coupling host atoms because of the different interatomic interactions between different chemical elements. In quantum crystals, however, the force constants are not simply coefficients in a Taylor series of the interatomic potential expanded in powers of the atomic displacements from equilibrium, but must be determined self-consistently by some averaging over the motions of the atoms. In a quantum crystal, therefore, a defect of different mass will induce force-constant changes, even though the defect may be chemically identical with the host atoms. This interesting effect was noted by Varma.[2] In this Letter we present a *quantum-mechanical* Green's function theory of the vibrations of dilute impure quantum crystals which is more general than Varma's semiclassical variation approach; we apply the theory to calculate the specific heat and thermal conductivity of dilute isotopic mixtures of solid He.

We find an equation of motion for a double-time thermally averaged Green's function

$$G_{ll'\alpha\beta}(t) = (2\pi/i\hbar)\theta(t)\langle[u_{l\alpha}(t), u_{l'\beta}(0)]\rangle \tag{1}$$

for displacements $u_{l\alpha}$ of the lth atom in the αth direction, as done by Elliott and Taylor[3] for harmonic systems. However, our Hamiltonian is the general one for two-body central interactions,[4,5]

$$H = \sum_{l\alpha} \frac{P_{l\alpha}^{\,2}}{2m_l} + \tfrac{1}{2}\sum_{l,j}{}' \exp(\vec{u}_{lj}\cdot\nabla_{lj})V(\vec{R}_{lj}). \tag{2}$$

The operator ∇_{lj} differentiates with respect to the difference between atomic coordinates $\vec{R}_{lj} \equiv \vec{R}_l - \vec{R}_j$, and $\vec{u}_{lj} \equiv \vec{u}_l - \vec{u}_j$. A complete equation of motion, which includes all anharmonic contributions, will be presented elsewhere. For this Letter we exhibit only the self-consistent harmonic approximation result; for the Fourier transform of the Green's function,

$$\omega^2 m_l G_{ll'\alpha\beta}(\omega) = \delta_{ll'}\delta_{\alpha\beta} + \sum_{j\gamma}\varphi_{lj\alpha\beta}G_{jl'\gamma\beta}, \tag{3}$$

where the effective force constant φ contains an approximate resummation of anharmonic terms,

$$\varphi_{lj\alpha\gamma} = \exp(\langle\vec{u}_{lj}\rangle\cdot\nabla_{lj} + \nabla_{lj}\cdot\overleftrightarrow{D}_{lj}\cdot\nabla_{lj})\,\partial^2 V(\vec{R}_{lj})/\partial R_{lj,\alpha}\,\partial R_{lj,\gamma}\ (l\neq j), \quad \varphi_{ll\alpha\gamma} = -\delta_{\alpha\gamma}\sum_{j\,(j\neq l)}\varphi_{lj\alpha\alpha}. \tag{4}$$