Electron-Hole Pair Creation by Atomic Scattering at Surfaces

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We report the direct measurement of the excitation of electron-hole pairs at a single-crystal InP (100) surface, induced by the scattering of ground-state Xe atoms over an incident energy range 2 eV $< E_i <$ 10 eV. Above $E_i \sim 3$ eV the yield is fitted well by an exponential dependence on E_i^{-1}. The incident-energy and angle dependence suggest the creation of a local thermal hot spot with fast electronic equilibration.

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We report the direct measurement of electron-hole pair ($e^- h^+$) excitations at a single-crystal surface created by the scattering of neutral ground-state Xe atoms. Xe beams are generated over an energy range 2 eV $< E_i <$ 15 eV by seeded molecular-beam techniques and are incident at an InP (100) surface. The transient current (yield) induced by Xe scattering is monitored as the incident energy and angle are varied. At normal incidence, the signal can be fitted by an exponential dependence on E_i^{-1} above 3 eV. At constant E_i, the signal falls steeply as the incident angle Θ_i moves away from the surface normal. We argue that the yield is consistent with a local thermal hot spot accompanied by rapid electronic equilibration. These measurements provide the first experimental basis for the understanding of the role of electronic excitations in the dynamics of thermal atomic and molecular processes at surfaces.

The dissipation of energy required for adsorption at surfaces is generally discussed in terms of lattice vibrational excitations.[1] In contrast, the role of electronic excitations has been only the subject of theoretical speculation.[2-5] We have previously shown that the exploitation of the electronic properties of a semiconductor, coupled with molecular-beam techniques, allows the electronic excitations to be monitored directly, using a rectified *p-i-n* Ge (100) diode.[6] However, the fragility of a rectified device, with respect to the mandatory cleaning and annealing requirements of such surface experiments, prevented us from measuring these excitations in a fruitful manner. Here we have used a compensated InP (100) crystal with Ohmic contacts which could be cleaned and moderately annealed without significant degradation of the electronic characteristics required for the measurements.

The essentials of the molecular-beam apparatus have been described elsewhere.[7] In brief, the Xe beam was formed out of a 100-μm aperture in a platinum nozzle which could be heated to 1300 °C. The Xe gas was diluted to concentrations as low as 0.1% from a premix of 10% Xe in He or 2% Xe in H_2. The beam was either square-wave modulated at typically 80 Hz for lock-in detection or chopped to ≈ 30-μsec pulses for time-of-flight or wave-form analysis.

The InP (100) crystal, containing $\approx 10^{16}$ cm^{-3} impurities, was Fe compensated to achieve a resistivity of $10^7 \Omega$ cm. Ohmic contacts consisted of 500 Å Ni under 500 Å Pt under 10^4 Å Au. Current-voltage scans at room temperature were linear, confirming the Ohmicity of the contacts over the temperature range of these experiments. The crystal was deployed in the manner of a photoconductor. A typical bias voltage was 10 V and the bias current ≈ 0.5 μA.

The crystal was etched with an HF-trichloroethylene solution and rinsed with deionized water. It was initially cleaned in vacuum with 1-keV Ar^+ bombardment and annealed to ≈ 220 °C. However, annealing after Ar^+ bombardment reduced the device resistance by a factor of $\approx 10^3$ (associated with depletion of P). The high resistance could be recouped by further sputtering without annealing. We found that neutral Xe bombardment at $E_i \approx 16$ eV was nearly as effective at cleaning the surface of major impurities as 1-keV Ar^+ ions, but with little loss of device resistance after annealing.[1] Auger spectra showed the InP surface to be reasonably clean after Xe bombardment and annealing, with less than 20% C and O, and traces of Cl and S. After processing, some evidence of the ordered $c(2\times 8)$ reconstruction reported for InP(100)[8] was found with He diffraction, but the pattern was neither sharp nor intense and not studied in detail at this point.

In Fig. 1, the transient current induced by a 30-μsec (FWHM) pulse of Xe impinging at 8 eV and normal incidence is plotted versus the flight time from the chopper for both an annealed and unannealed Xe-cleaned surface. In both cases there is a small peak at zero time which represents the photocurrent induced by photons originating from the hot nozzle. At approximately 60 μsec later the Xe beam arrives at the crystal and a second and larger current transient is observed. The Xe-induced current for the annealed surface is an order of magnitude larger than that for a typical unannealed surface. The Xe-induced and photocurrent wave forms are essentially the width of the chopper function, and thus indicative of a fast collection process on the time scale of these measurements (≈ 30 μsec). For the unannealed surface, an extended tail is observed which we think is characteristic of thermal-energy surface traps. In addition, the ratio of

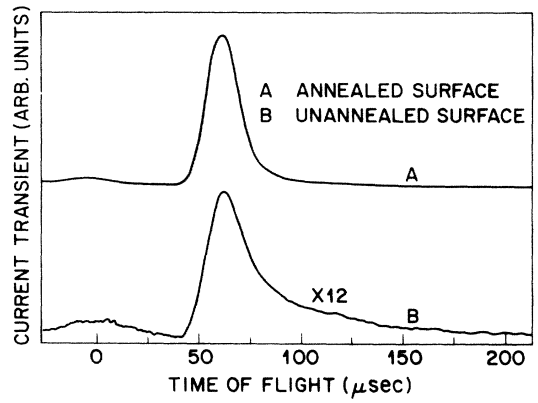

FIG. 1. Xe-induced current transient on InP(100) for $E_i \sim 8$ eV and $\Theta_i = 0$ for a 30-μsec pulse width. The small peaks at $t \sim 0$ are due to light from the heated nozzle. The peaks at $t \sim 60$ μsec are Xe induced.

the Xe-induced current to the photon-induced current is increased by about a factor of 3 after a typical anneal. This indicates that the Xe-induced e^-h^+ signal is dominated by the interaction at the surface, in contrast to the photon yield which essentially is due to bulk processes. The Xe-induced current is orders of magnitude larger than that expected for bulk heating.

In Fig. 2 we plot the signal on a logarithmic scale vs E_i at normal incidence as measured with a lock-in amplifier. The open and closed points represent measurements at equal E_i but for beams formed at 1% and 2% Xe dilution in H_2, respectively. The nozzle temperature was varied to achieve the same energy for the different mixtures. Each pair results from two different nozzle temperatures and thus different photon fluxes. The agreement confirms the minor contribution to the lock-in measurement of photons or excited or ionic species produced by the nozzle. The Xe-induced signal becomes observable above $E_i \sim 2$ eV (the band gap ~ 1.4 eV) and rises rapidly with increasing energy up to $E_i \approx 9$ eV. Above 9 eV significant ion ejection (In^+) was observed from the surface[9] and this interfered with the e^-h^+ measurement (In^+ ejection corresponds to e^- injection).

To obtain the absolute e^-h^+ excitation yield Y per Xe atom the collection efficiency must be estimated. It is dependent on carrier recombination rates and transport, which are not known for this crystal. We obtain an order-of-magnitude estimate from the following argument. The current transient ΔI at a bias voltage V corresponds to an increased conductance of the sample ΔC_T. We associate this with the conductance change of the smaller illuminated area ΔC_{Xe}, which from the geometry of the sample is

$$\Delta C_T = \tfrac{3}{8}\Delta C_{Xe} = (3wd/8l)\Delta\sigma_{Xe}$$
$$= (3wd/8l)q(\mu_n + \mu_p)\Delta n. \quad (1)$$

The beam impacts an area $w \times l$, d is the sample thickness, and $\Delta\sigma_{Xe}$ is the conductivity change of the illuminated area. Δn is the increased carrier density created by Xe impact, q is the electronic charge, and $\mu_n + \mu_p$ is the sum of the electron and hole mobilities. We assume steady-state conditions in the exposed region so that the rate of carrier generation due to Xe impact, $F_{Xe}Y$, at a Xe flux F_{Xe}, is quickly balanced by the increased recombination rate $R = (\tau^{-1})\Delta N = (\tau^{-1})\Delta n\, wdl$, where τ is a characteristic time and ΔN is the increase in the number of carriers in the illuminated volume. This yields

$$Y = 8\Delta I l^2/3V\tau F_{Xe} q(\mu_n + \mu_p). \quad (2)$$

Taking $\mu_n + \mu_p \sim 5\times 10^3$ cm^2 V^{-1} sec^{-1} at $E_i = 9$ eV, we obtain $Y = (3\times 10^{-10}\ \text{sec})\ \tau^{-1}$.

τ is not known for this compensated InP crystal. For many doped InP crystals τ is of the order of a few nanoseconds. With large uncertainties we estimate that the e^-h^+ excitation probability per Xe atom at $E_i = 9.5$ eV is of the order of $Y = 0.3$, taking $\tau \sim 10^{-9}$ sec.

For the energy range of these experiments, we have measured the total energy transfer from time-of-flight

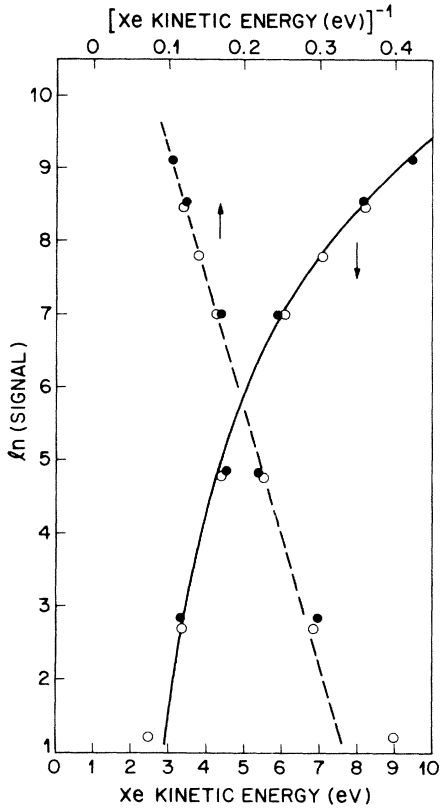

FIG. 2. Xe-kinetic-energy dependence of the collision-induced conductivity in annealed InP(100) at $T_s = 300$ K and $\Theta_i = 0$. Results are normalized to Xe flux and plotted vs E_i (lower scale) or E_i^{-1} (upper scale). Open and closed circles were measured with use of 2%- and or 1%-Xe mixtures with H_2, respectively.

measurements for InP(100) at $\Theta_i = 30°$, as well as from other crystals [GaAs(110), Ge(100), Ag(100)] for a wide range of incident angles.[9] The average Xe energy loss for all of these measurements is large and ranges up to $\approx 90\%$ at the higher energies ($E_i \approx 9$ eV), and nearly scales with the energy associated with normal motion, i.e., $\Delta E \approx E_i \cos^2\theta_i$. On the basis of these results we expect for $E_i = 9$ eV and $\Theta_i = 0$ an average energy transfer of ≈ 7.5–8.5 eV. Thus, our rough estimate of the yield at $E_i = 9$ eV suggests that 5% of the Xe energy loss goes into $e^- h^+$ excitations, on the assumption of threshold electronic excitations of 1.4 eV.

We have tried unsuccessfully to observe photons emanating from geminate $e^- h^+$ or bulk recombination of the Xe-collision-induced carriers for both the compensated InP (100) crystal discussed here and on a Sn-doped (8×10^{17} cm^{-3}) InP (100) crystal, selected to enhance photoluminescence.[10] We estimate the maximum photoemission probability per Xe collision at $E_i = 9$ eV to be less than 10^{-5}, indicating that most Xe-induced carriers recombine nonradiatively.

In Fig. 3 we plot the dependence of the $e^- h^+$ signal A on the Xe incident angle Θ_i at $E_i = 6.2$ eV for the annealed and unannealed "clean" surface. The data for the annealed surface (open points) fall sharply with incident angle compared to the data from the unannealed surface. The solid line is the expectation for the annealed surface if the angle dependence arises from the scaling of A with the energy associated with normal motion $E_i \cos^2\Theta_i$, i.e., $A(\Theta_i, E_i = 6.2 \text{ eV}) = A(0, E_i \cos^2\Theta_i)$. The weaker dependence of A on Θ_i for the unannealed surface is in the direction expected for a distribution of local surface normals for a roughened surface.

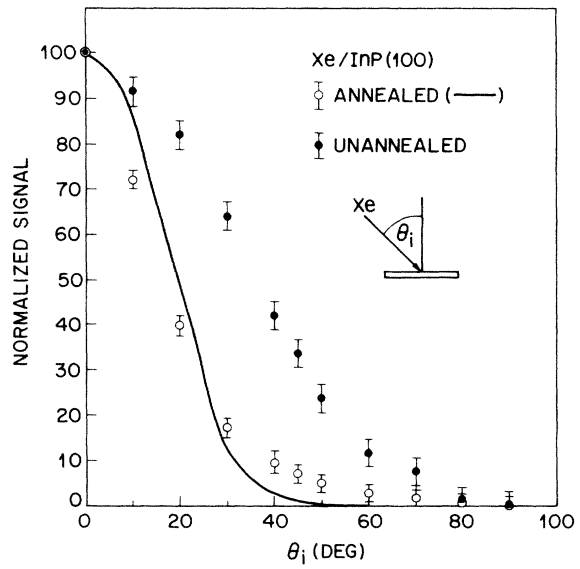

FIG. 3. Incident-angle dependence of the Xe-induced conductivity signal. $E_i = 6.2$ eV and $T_s = 300$ K. The line is derived from the energy dependence at $\Theta_i = 0$ on the assumption $Y \propto E_i \cos^2\theta$.

The near scaling of both the yield and the total energy transfer with $E_i \cos^2\Theta_i$ implies that the $e^- h^+$ yield is determined by the deposited energy. We argue that this is consistent with what may be expected for a local thermal hot spot created by the initial energy deposition of the scattering Xe atom.

Consider that the Xe approaches the surface at nearly the solid speed of sound over much of the experimental energy range. Upon the initial impact the lighter substrate atom recoils classically at a higher speed than the Xe, rebounds from its neighbors, and rehits the still incoming Xe atom before a significant fraction of the energy flows out of the "first shell" of nearest neighbors. Most of the energy is transferred in this initial part of the collision and must be contained within a local region of a few atoms. We take the high-temperature heat capacity $C_v = 3nk$, where n is the number of participating atoms, to define a local effective temperature rise $\Delta T_e = \Delta E_{Xe}/3nk$. The Boltzmann fraction of electrons which lies above the band gap from this temperature rise is $\exp[-E_{bg}/k(\Delta T_e + T_0)]$. Ignoring entropy factors we estimate the excitation yield for $\Delta T_e \gg T_0$ as

$$Y \sim n \exp(-3nE_{bg}/\Delta E_{Xe}) \approx n \exp(-3nE_{bg}/E_i). \quad (3)$$

In Fig. 2 we demonstrate the linear relation between $\ln Y$ and E_i^{-1}. For values of $E_i > 3$ eV we extract a slope 35.5 eV. On the assumption that $E_{bg} = 1.4$ eV is the appropriate excitation-energy requirement, this corresponds to $n = 8.5$ and a value of $Y = 0.2$, consistent with our experimental estimate and with the idea of a localized transient hot spot. Note that in Eq. (3) the electrons are assumed to equilibrate rapidly to the local energy in the region of Xe impact compared to all other relevant time scales. In addition, the carriers do not flow out of the disturbed region rapidly compared to the local thermal relaxation rate, so as to cool the region. A large fraction of them remain as the lattice begins to relax and drift away as carriers, deexciting at the normal bulk or surface carrier relaxation rates.

If the yield is considered to be the result of a definable rate process, one could write an equation based on an excitation-rate constant defined as $k(T) = \tau_{ep}^{-1} \times \exp(-E_{bg}/kT)$, where τ_{ep} is a characteristic electron-phonon equilibration time. The yield would then be postulated to be the time integral over the $n(t)$ excited atoms at a temperature $T(t) = \Delta E/3kn(t) + T_0$, i.e.,

$$Y = \int_0^\infty \frac{1}{\tau_{ep}} n(t) \exp\left[-\frac{E_{bg}}{3n(t)} + kT_0\right] dt. \quad (4)$$

As t increases $n(t)$ increases and the effective temperature rise $\Delta T(t) = \Delta E/3kn(t)$ decreases. If this integral is assumed to be dominated by its short-time (t') value,

then

$$Y=\frac{t'}{\tau_{ep}}n(t')\exp\left[\frac{-3n(t')E_{bg}}{E_i}\right]. \quad (5)$$

Again the slope of the $\ln Y$ vs E^{-1} yields $n(t')\sim 8.5$, whereas the yield is now $Y=0.2t'/\tau_{ep}$, and not well defined. The argument for a local hot spot should not hold at the lower impact energy range.

From simple classical mechanics the initial energy transferred from Xe to a single substrate atom can be considerably greater than its binding energy. The initial electron excitation probability may reasonably be expected to be high, as in sudden bond breaking or equivalently severe bond compression. It may be only in the subsequent redistribution of the target-atom energy to its neighbors that the thermalization of the number of excited electrons occurs. In addition some fraction of the yield may originate from surface states associated with defects or impurities for which the threshold energy is considerably lower than E_{bg}. In principle the dependence of the yield on the initial temperature T_0 should permit the effective threshold energy to be determined. We have measured an increase in the yield with increasing T_0 but cannot interpret the results quantitatively since the temperature dependences of the mobility, surface order, and collection efficiency are not understood.

In summary, we have shown that the excitation of electron-hole pairs at a surface by neutral particles can be measured directly by the scattering of hyperthermal Xe atoms at an InP (100) surface. These measurements provide the first experimental evidence for the nature and extent of participation of electronic excitations in thermal gas-surface interactions.

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