Dynamical Interaction of Surface Electron-Hole Pairs with Surface Defects: Surface Spectroscopy Monitored by Particle Emissions

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Excitation spectra and optical anisotropy for laser-induced Ga^0 emission initiated by defects on GaAs(110) surfaces have been measured. It is found that the Ga^0 emission yield is enhanced sharply when the photon energy increases across both 1.87 and 2.55 eV and that the enhancement is much larger for photons polarized parallel to the $[1\bar{1}0]$ direction than for those polarized perpendicular. The result indicates that electron-hole pairs on the surface are particularly effective in the defect-initiated emission of Ga^0.

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The surface states of semiconductors have been a topic of intense experimental and theoretical investigation and extensive work has been carried out to reveal the electronic structures of many semiconductors [1,2]. So far, however, studies are mostly confined to structural studies and almost no information has been obtained on the dynamical properties of two-dimensional (2D) electron-hole (*e-h*) pairs, of which motion is restricted in the surface state. The surface recombination velocity [3] is relevant to the *e-h* pairs on the surface, but it has been understood only phenomenologically. Further microscopic features of the dynamics of the 2D electron-hole pairs on the surface, such as lifetime, interaction with defects, and conversion to bulk (3D) electron-hole pairs, are problems of fundamental interest.

Recently high-sensitivity measurements of laser-induced emission of Ga atoms from GaP surfaces below the ablation threshold have revealed that the emission is of electronic origin and initiated by defects [4–6]. According to these experimental results, repeated irradiation at the same spot of the cleaned GaP (110) and $(\bar{1}\bar{1}\bar{1})$ surfaces with laser beams below the ablation threshold reduces the emission yield first rapidly and then slowly. The slow component persists over thousands of shots of laser pulses. The rapidly decaying component has been ascribed to the breaking of the bonds of adatoms, and the slowly decaying component to the emission of atoms at kink sites [4]. Furthermore, it has been shown that the emission is observed by irradiation with photons below the band-gap energy (2.261 eV), but it is diminished almost completely as the photon energy increases across the band-gap energy [7]. This result indicates that the emission yield depends on the type of excitation.

Generally, the emission of atoms on the surface by electronic transitions occurs due to breaking of the bond by local electronic excitation. Since the fundamental electronic excitation produces delocalized *e-h* pairs or excitons in nonmetallic solids, localization of the excitation energy is the initial step for the emission of atoms [8]. For instance, the self-trapping of an exciton near the surface in alkali halides [9,10] is considered to form a MGR- (Menzel-Gomer-Redhead-) type [11,12] antibonding adiabatic potential energy surface to cause emission of constituent atoms. The result that laser-induced emission from semiconductors is defect initiated is interpreted as defects acting as localization sites of the fundamental excitation [5,10]. Since the emission measurements are highly sensitive, capable of detecting 10^{-5} monolayer atom [6], the technique is most suited for investigating the dynamic interaction of electron-hole pairs with defects on the surface.

Because of the superlinear yield-fluence relation [4,5], the mechanism of the laser-induced defect-initiated emission from GaP is still controversial [10]. Apart from the detailed mechanism of the emission, since the emission of Ga atoms is not induced without the localization of the fundamental excitation, a study of the excitation spectrum is considered to yield a clue to understanding the dynamic interaction of the electron-hole pairs near the surface with defects. GaAs is of the most interest for studies of this type, since the transitions between the occupied and unoccupied surface states near the edge are indirect. The number of 2D electron-hole pairs can be increased with increasing photon energy above the band-gap energy and their contribution to the emission can be studied in detail.

This paper reports measurements of the excitation spectrum for laser-induced Ga^0 emission from GaAs and gives direct evidence for the dynamic interaction of 2D *e-h* pairs with defects on the GaAs(110) surface.

In order to obtain the excitation spectra for laser-induced Ga^0 emission, we employed a combination of varying the temperature T of the specimen and varying the energy $h\nu$ of the laser photons: The temperature dependence of Ga^0 emission was measured with laser pulses of several wavelengths. The obtained emission yield was plotted as a function of the difference between the photon energy ($h\nu$) and the band-gap energy $[E_g(T)]$ at the temperature. A scaling factor was used multiplied so that the yields at the same value of $h\nu - E_g(T)$ obtained at two different wavelengths are identical. This method facilitates the acquisition of the excitation spectra

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in spite of the change in the laser-beam profile when the wavelength is changed. The same method was used by Okano *et al.* for GaP [7].

The emission of Ga^0 atoms induced by pulsed laser irradiation was measured using resonant ionization spectroscopy as reported elsewhere [4,5]. The laser beams of 28 ns duration for exciting the surface ("pump" laser) and for ionizing the emitted Ga^0 ("probe" laser) were generated by excimer-laser–pumped dye laser systems. The "pump" laser beam was incident 45° from the surface normal and its fluence is in a range of 10 mJ/cm^2, far below the ablation fluence ($\sim$100 mJ/cm^2). The photon energy of the probe laser was tuned to a half of the $^2P_{1/2}$-$^2D_{3/2}$ energy of Ga atoms and the frequency-doubled beam was used for excitation and the fundamental beam for ionization of the excited Ga atoms. The probe laser pulses were delayed by 3 μs from the pump laser pulses and passed parallel to the sample surface at a distance of 2.0 mm. The ionized Ga ions were detected by an electron multiplier. A calcite polarizer was used to polarize the "pump" beam and a specimen was rotated with respect to the direction of polarization to measure the effect of polarization.

The GaAs(110) surface was treated by repeated cycles of Ar^+ bombardment (500 eV, 3.0 μA/cm^2) and annealing at 800 K for 3 min. After the treatments a sharp (1×1) low energy electron diffraction (LEED) pattern was observed and no residual impurities on the surface were detected by Auger electron spectroscopy (AES). Observation of the Ga-As ratio by AES and the presence of the sharp LEED pattern assures the stoichiometry of the surface. The specimen was attached to a tantalum sample holder and its temperature was varied by changing the electric current through a tungsten filament attached to the holder. The temperature was monitored by Alumel-Chromel thermocouples mounted to the holder. Similarly the GaP surfaces, repeated irradiation at the same spot of the cleaned GaAs surface with laser pulses produces the rapidly decaying and persistent components. In obtaining the excitation spectrum for Ga^0 emission, we first eliminated the former component by repeated irradiation and measured the excitation spectrum for the persistent component.

Typical results of the temperature dependence for laser beams with several photon energies are shown in Fig. 1. No polarizer was used in this experiment. Evidently, the yield increases as the temperature increases, but more slowly for lower photon energies. Similar curves in nearly the same temperature range were obtained in the photon-energy range between 1.41 and 2.53 eV. A plot of the yield as a function of $h\nu - E_g(T)$ is shown in Fig. 2. $E_g(T)$ was calculated using the experimental relation of Panish and Casey [13]:

$$E_g(T) = 1.522 - 5.8\times10^{-4}T^2/(T+300)\,.$$

Since all data obtained with laser beams of different photon energies merge into a single curve, we consider that the technique can be used for obtaining the excitation spectrum. The curve can be regarded as the excitation spectrum for the laser-induced Ga^0 emission from the GaAs(110) surface. The Ga^0 emission yield for photon energies just below E_g is essentially zero in this fluence range. The yield increases as $h\nu - E_g(T)$ increases and becomes constant around 100 meV above E_g. It is further enhanced when $h\nu - E_g(T)$ increases across both 0.42 and 1.10 eV. Apart from the three stepwise in-

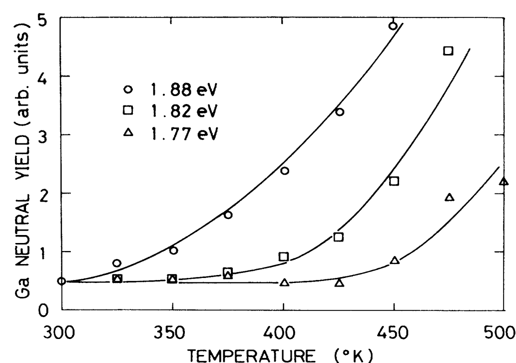

FIG. 1. The temperature dependence of Ga^0 emission yield from the GaAs(110) surface by pulsed laser beams of photon energies indicated in the figure. Each curve was obtained for a spot on the surface where irradiation was repeated until the rapidly decaying component disappeared.

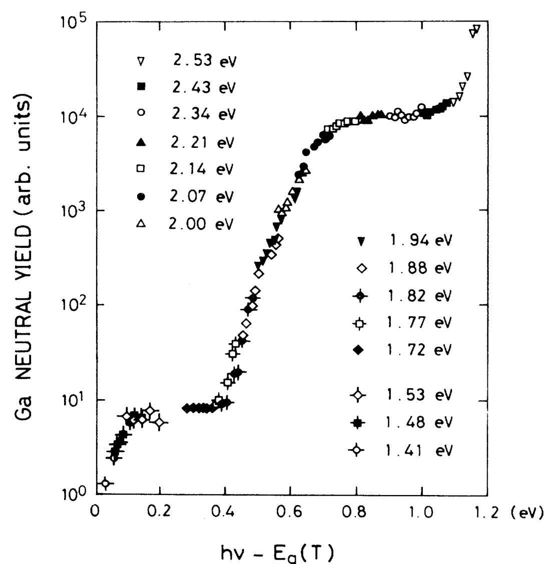

FIG. 2. A replot of the yield-temperature relations obtained with unpolarized laser beams of various photon energies between 1.41 and 2.53 eV, as a function of $h\nu - E_g(T)$, where $h\nu$ is the photon energy and $E_g(T)$ is the band-gap energy at temperature T. A scaling factor was used so that the yields at the same value of $h\nu - E_g(T)$ obtained at two different photon energies are identical.

creases of the yield, the dependence of the yield on $h\nu - E_g(T)$ is extremely small.

In order to see whether the steps observed above are related to the transitions involving the surface states, we measured the optical anisotropy for the excitation spectrum. Figure 3 shows the temperature dependence of the Ga^0 emission yield by laser pulses polarized parallel and perpendicular to the $[1\bar{1}0]$ direction on the GaAs(110) surface, obtained for photon energies of 1.88 and 2.53 eV. The former photon energy corresponds to the onset of 0.42 eV, while the latter corresponds to the onset of 1.10 eV. It is clear that the yield for excitation with photons polarized parallel to the $[1\bar{1}0]$ direction increases steeply as the sample is heated from 300 to 500 K, while there is essentially no increase for photons polarized perpendicular. The present results indicate that both steps are due to the optical transitions, of which the dipole moments are strongly polarized along the $[1\bar{1}0]$ direction, the direction of the Ga-As chains on the surface plane. Since the GaAs lattice has a cubic symmetry, the result indicates that the Ga^0 emission is strongly enhanced by the onset of the transitions involving the occupied surface band.

In order to compare the location of the steps with existing data on the transitions involving the surface bands, we show the schematic surface band structure of the GaAs(110) surface in Fig. 4. Also shown are possible optical transitions involving surface states: T_1, the transition from the occupied surface band to the unoccupied surface band; T_2, from the occupied surface band to the bulk conduction band; and T_3, from the valence band to the unoccupied surface band. According to theoretical calculation by Manghi *et al.* [14], the dipole moments of the transitions T_1 and T_2 are strongly oriented along the $[1\bar{1}0]$ direction, while that for T_3 is almost isotropic. Thus we assign that the step at $h\nu - E_g(T) = 0.42$ to the T_2 transition and that at 1.10 eV to the T_1 transition.

The values of T_1, T_2, and T_3 at room temperature can be derived using the experimental data on normal and inverse photoemission. A photoemission experiment shows that the difference between T_2 and $E_g(T)$ is 0.5 ± 0.2 eV [15]. An inverse photoemission experiment [16] shows that $T_3 = 2.0 \pm 0.1$ eV, while $E_g(300\ \mathrm{K}) = 1.44$ eV. Thus $T_1 - E_g(T) = T_3 + T_2 - 2E_g(T) = 1.06 \pm 0.3$ eV. Evidently, the present results fall within the experimental error of previously obtained values. According to the inverse photoemission results, $T_3 - E_g(T) = 0.56$ eV. We consider that the wiggle near 0.5 eV corresponds to the T_3 transition, although the polarization experiment was not successful because of the overlap with the T_2 transition.

We presumed that the variation of the surface band-

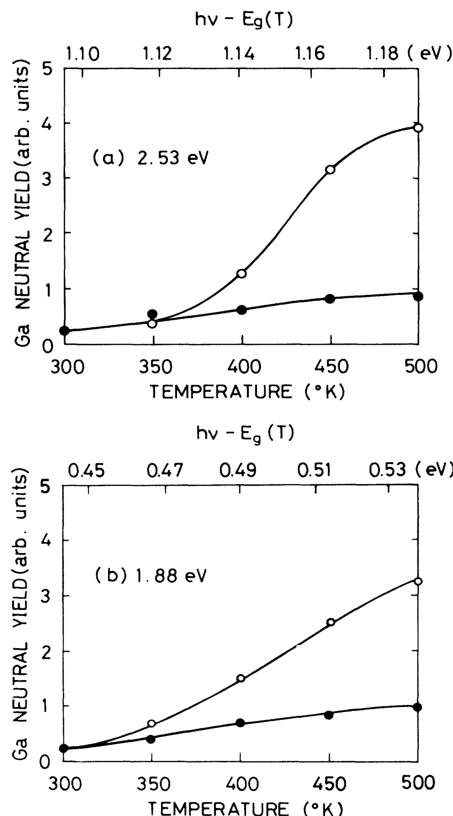

FIG. 3. The temperature dependence of Ga^0 emission yield by pulsed laser beams polarized parallel (open circles) and perpendicular (filled circles) to the $[1\bar{1}0]$ direction on the GaAs(110) surface for photon energies of (a) 2.53 eV and (b) 1.88 eV.

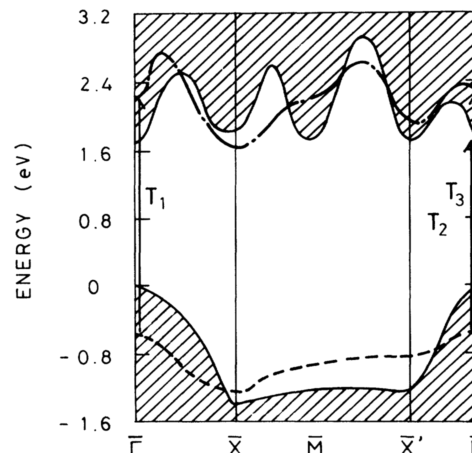

FIG. 4. A schematic band structure of the GaAs(110) (1×1) surface. The dashed line shows the top of the highest occupied surface band obtained from photoemission measurement, the dash-dotted line indicates the theoretical results for the bottom of the lowest unoccupied surface band, and solid lines show the bulk band structures. T_1 and T_2 are the electronic transitions at the $\bar{\Gamma}$ point from the occupied surface band to the unoccupied surface band and to the bulk conduction band, respectively, and T_3 shows that from the bulk valence band to the unoccupied surface band (from Ref. [2]).

gap energy with temperature is parallel to that of the bulk band gap. Since the change in the lattice constant is of primary concern to these temperature dependences, we consider that this assumption is appropriate. The result that experimental data obtained with laser beams of different photon energies merge on a single curve in error by 50 meV as indicated in Fig. 2 supports the presumption. An error in the measured value of temperature of 20 K corresponds to an error in the energy of only ± 10 meV.

The results that the Ga^0 emission yield is enhanced by the T_1 and T_2 transitions indicate that the 2D *e-h* pairs are effective in producing the emission; the electron-hole pairs produced by the T_2 transition can be regarded as 2D *e-h* pairs, since the electrons in the bulk conduction band are attracted to the holes, whose motion is confined to the surface. It is still premature to make further quantitative discussions on the magnitudes of the steps. First, the contribution of the T_3 transitions is not decided. Second, the contribution to the emission of 3D *e-h* pairs, of 2D *e-h* pairs with holes in the bulk valence band, and of 2D *e-h* pairs with holes in the occupied surface band should be distinguished. If the contribution of these three types of excitation is assumed to be the same, each transition increases the yield by a factor of 10–40. In view of the superlinear yield-fluence relation, the result is not surprising.

The present result that 2D *e-h* pairs induce the Ga^0 emission is consistent with the observation for the GaP(110) surface [7]. For GaP, it has been found that the emission yield is reduced when the photon energy increases across the bulk band edge. Since the surface band-to-band transition below the bulk band edge is allowed and the bulk band-to-band transition near the band edge is forbidden, the result for GaP implies that 2D *e-h* pairs having energies of bulk *e-h* pairs are transformed to 3D *e-h* pairs by phonon scattering.

In conclusion, we have demonstrated that 2D *e-h* pairs make a substantial contribution to defect-initiated emission on GaAs(110) surfaces, indicating the dynamic interaction between 2D *e-h* pairs and defects on surfaces. As discussed elsewhere, we consider that the recombination of an electron-hole pair at a defect (kink sites) on the surface produces a metastable state, which can absorb photons further and is brought to a nonbonding state [5]. The present investigation indicates that the interaction of 2D electron-hole pairs with the defects is the most crucial step. The present investigation demonstrates also that measurements of excitation spectra for atomic emission are of use for locating electronic transitions involving the surface bands.

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[1] G. V. Hansson and R. I. G. Uhrberg, Surf. Sci. Rep. **9**, 197 (1988).

[2] F. J. Himpsel, Surf. Sci. Rep. **12**, 1 (1990).

[3] R. A. Smith, *Semiconductors* (Cambridge Univ. Press, Cambridge, 1978).

[4] K. Hattori, A. Okano, Y. Nakai, N. Itoh, and R. F. Haglund, Jr., J. Phys. Condens. Matter **3**, 7001 (1991).

[5] K. Hattori, A. Okano, Y. Nakai, and N. Itoh, Phys. Rev. B **45**, 8424 (1992).

[6] Y. Nakai, K. Hattori, A. Okano, N. Itoh, and R. F. Haglund, Jr., Nucl. Instrum. Methods Phys. Res., Sect. B **58**, 452 (1991).

[7] A. Okano, K. Hattori, Y. Nakai, and N. Itoh, Surf. Sci. **258**, L671 (1991).

[8] N. Itoh and K. Tanimura, J. Phys. Chem. Solids **51**, 717 (1990).

[9] M. Szymonski, in *Desorption Induced by Electronic Transitions*, edited by G. Betz and P. Varga (Springer-Verlag, Berlin, 1990), p. 270.

[10] N. Itoh, Y. Nakai, K. Hattori, A. Okano, and J. Kanasaki, in Proceedings of the Fifth Workshop on Desorption Induced by Electronic Transitions, DIET V, 1992 (Springer-Verlag, New York, to be published).

[11] D. Menzel and R. Gomer, J. Chem. Phys. **41**, 331 (1964).

[12] P. Readhead, Can. J. Phys. **42**, 886 (1964).

[13] M. B. Panish and H. C. Casey, Jr., J. Appl. Phys. **40**, 163 (1969).

[14] F. Manghi, E. Molinari, R. Del Sole, and A. Selloni, Phys. Rev. B **39**, 13005 (1989).

[15] A. Huijser, J. van Laar, and T. L. van Rooy, Phys. Lett. **65A**, 337 (1978).

[16] D. Straub, M. Skibowski, and F. J. Himpsel, Phys. Rev. B **32**, 5237 (1985).