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Characterization of surface defects by means of laser-induced Ga^0 emission from GaP surfaces

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Abstract. We have carried out high-sensitivity measurements of the emission of Ga^0 neutrals from a clean GaP(110) surface induced by laser pulses of subgap photon energies. We found that, below a sharp threshold laser fluence for evolution of surface damage, the emission yield of Ga^0 atoms decreases, following two exponential functions, with repeating pulses of the same fluence. These two decays are ascribed to the ejection initiated by defects of two different types. These measurements are shown to be useful for characterizing defects of extremely small concentration.

There is increasing interest in identifying, characterizing and controlling small concentrations of surface defects over a relatively large area in electronic and photonic materials. This capability is important both for technological reasons, as in the fabrication of multiple-quantum-well devices, and for basic scientific studies of surface electronic structure. However, most current techniques for microscopic surface analysis do not have this capability. For example, scanning tunnelling microscopy [1] has an extremely high spatial resolving power but can only evaluate defects quantitatively over a relatively small surface area.

In this paper we report the first demonstration that laser-induced particle emission monitored by resonance ionization mass spectroscopy successfully differentiates between several types of defect in the topmost atomic layer of a GaP specimen. In addition, we show that certain of these defects can be eliminated from the surface by prolonged irradiation of the surface without producing crystallographic damage. Finally, we show that this same technique is able to provide significant clues to the nature of the defects responsible for laser-induced surface damage above a certain fluence threshold.

The specimens used in this experiment were n type (S-doped) GaP single crystals measuring 10 mm × 10 mm × 2 mm. The wide face parallel to the (110) plane was mechanically polished, chemically etched and finally cleaned by Ar^+ ion bombardment and thermal annealing in ultra-high vacuum (base pressure, less than 2×10^{-8} Pa) [2, 3]. After cleaning, the surface showed a clear (1 × 1) low-energy electron diffraction (LEED) pattern and no Auger signal due to surface contaminations was detected. The surface was bombarded by an excimer-pumped dye laser at a wavelength of 600 nm and a pulse width of 28 ns. The laser beam of this wavelength is capable of exciting the

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electrons in the valence band to the unoccupied surface states located 0.3 eV below the conduction band [4] but not of inducing band-to-band transitions. Hence the heating of the surface layer is extremely small [5]. This 'pump' laser beam, which was made as uniform as possible using apertures and lenses, was incident on the specimen at an angle of 45° from the surface normal. The beam spot on the surface was 0.5 mm in diameter.

Emitted neutrals were observed with high sensitivities using the resonance ionization spectroscopy (RIS) technique [6] as reported elsewhere [7]. Frequency-doubled light from a second excimer-pumped dye laser was used to excite the $^2P_{1/2}$ to $^2D_{3/2}$ transition of Ga neutrals, while the fundamental beam from the same laser (at 574.82 nm) ionized excited Ga neutrals. The RIS laser was triggered about 5 μs after the pump (desorption) laser and passed parallel to the surface at a distance of 2.0 mm. Ga^+ ions were detected with a channeltron, the signals of which were stored in a microcomputer.

We measured the Ga^0 yield from the GaP(110) surface induced by repeated irradiation with laser pulses of a fixed laser fluence on the same spot. Figures 1(*a*) and 1(*b*) show typical results for the yield Y of Ga^0 neutrals per pulse as a function of the number n of laser shots at laser fluences of 1.0 J cm^{-2} and 1.2 J cm^{-2}, respectively. A previously unirradiated spot of the sample was bombarded repeatedly by laser beams of each fluence. The fluctuation of the fluence of the laser pulses at each 'fixed' fluence was about 5%. As seen from figure 1(*a*), Y decreases initially with increasing n, approximately following an exponential relation, and reaches nearly a constant value, which decreases very slowly and lasts over 8000 pulses. The ordinate is given in arbitrary units, of which unity approximately corresponds to the removal of atoms in a 10^{-6} monolayer. We refer to the decreasing component as the A component and the nearly constant component as the S component. The LEED pattern obtained on the laser-focused spot was unchanged after 8000 pulses.

On the other hand, above a fluence of 1.2 J cm^{-2}, a rapid increase in Y with increasing n is seen as shown in figure 1(*b*). We note a remarkable difference in the Y–n relation by changing the laser fluence by only 20% across a critical fluence I_D of 1.1 J cm^{-2}. Above the critical fluence, each spot of the LEED pattern became weaker after several hundreds of laser shots. Thus we ascribe the increase in Y with increasing n (referred to as the D component) to the evolution of damage on the surface. We note that at the initial stage of evolution the number of atoms emitted by each laser pulse is small, nearly of the order of 10^{-6} monolayer, and that the number of atoms starts to increase if initial damage is produced on the surface. Thus it is clear that the mechanism of initial damage occurs without emitting a large number of atoms and hence is purely electronic.

Since the emission yield of Ga atoms is reduced by repeating laser pulses, even though the surface remains undamaged, the A component in the Y–n relation is undoubtedly due to defect-initiated particle emission. We assign also the S component to defect-initiated particle emission for the following reasons. First no change was observed in the LEED pattern after 8000 shots. Second, no increase in Y was observed even at $n = 8000$, while an increase in Y is seen at $n = 20$ for a fluence larger by only 20%. Suppose that both the S and the D components were due to the evolution of the damage on the surface, then we should see a rapid increase in the probability of destruction of perfect sites as the laser fluence is increased; indeed the yield should follow about the thirtieth power of the laser fluence if Y is a power function of the laser fluence. Since such a high power dependence is unrealistic, we consider that S emission and damage mechanisms are distinct. Thus it is clear that two completely different types of defect can be differentiated by measuring the dependence of the yield on the number of shots.

The number $dN_E(n)/dn$ of atoms emitted by a laser pulse for the A and S components can be fitted to exponential functions $Y_0 \exp(-\alpha n)$, with $Y_0 = 3.0$ (arbitrary units), $\alpha =$

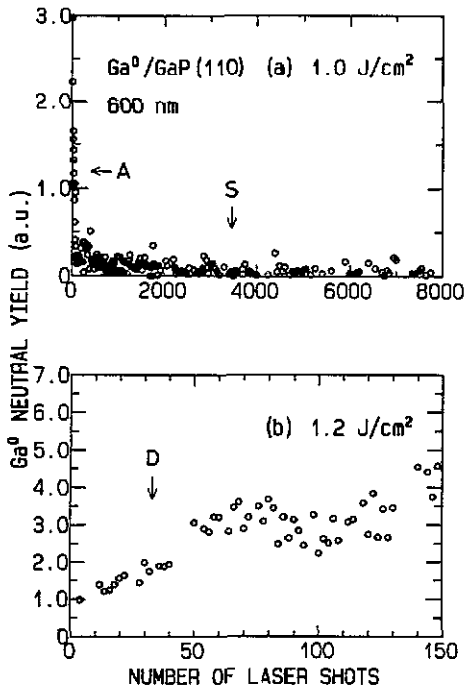

Figure 1. Plots of Ga^0 yield from the GaP(110) surface as a function of the number of laser shots at fluences of (*a*) 1.0 J cm^{-2} and (*b*) 1.2 J cm^{-2}. A new spot was exposed to the laser beam at the start of the experimental run for each fluence and the same spot was irradiated repeatedly. Three typical features of the Ga^0 yield as a function of the number of shots, decreasing, constant and increasing, are referred to as A, S and D components, respectively.

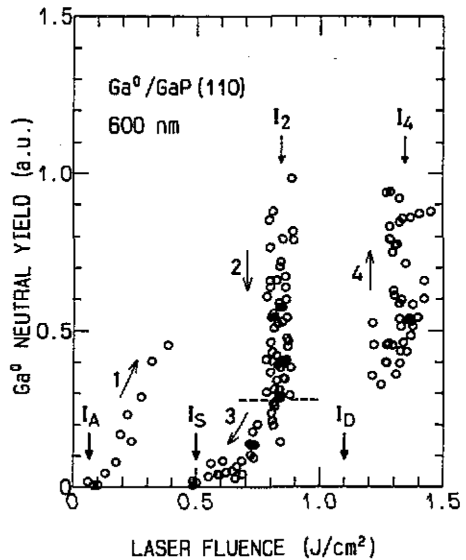

Figure 2. Dependence of Ga^0 yield on the laser fluence for sequential irradiation of the GaP(110) surface: data 1, the laser fluence was increased gradually; data 2, the laser fluence was kept constant at $I_2 = 0.85$ J cm^{-2}; data 3, the laser fluence was decreased gradually; data 4 the laser fluence was kept constant at $I_4 = 1.35$ J cm^{-2}. The arrows beside the plots show the direction of the change by the sequential irradiation. The threshold laser fluences I_A, I_S and I_D (see text) are indicated by vertical arrows.

1.1×10^{-2}, and $Y_0 = 0.12$ (arbitrary units), $\alpha = 7 \times 10^{-5}$, respectively. If the emission of atoms is initiated by defects, the number of atoms emitted per laser pulse is proportional to the defect concentration on the surface: $\mathrm{d}N_E(n)/\mathrm{d}n = \eta N_D(n)$, where η is the yield and $N_D(n)$ is the number of defects after the nth shot. It follows that $N_D(0) = Y_0/\eta = (Y_0/\alpha)(\alpha/\eta)$. We obtained the ratio for Y_0/α for the S and A components to be 6.3.

The laser-induced particle emission varies superlinearly with laser fluence [8, 9]. Therefore, one can define an apparent threshold laser fluence above which the particle emission is observed. In order to find the threshold laser fluence for particle emission initiated by each type of defect, we carried out an experiment, for which the results are shown in figure 2. In this experiment we irradiated a new spot on the surface starting from low laser fluences and obtained Y as a function of fluence, as shown by data 1. The threshold laser fluence I_A of 0.07 J cm^{-2} can be ascribed to the A component. Next we repeated irradiation at fluences near $I_2 = 0.85$ J cm^{-2}, where Y was decreased as shown by data 2, removing the A component remaining after irradiation at low fluences. When

Y became almost constant, we reduced the laser fluence. Below a threshold laser fluence of $I_S = 0.5\ \mathrm{J\,cm^{-2}}$, the yield vanished, as shown by data 3. We consider that this is the threshold fluence for the S component. When the laser fluence was fixed at $I_4 = 1.35\ \mathrm{J\,cm^{-2}}$ above I_D, Y was increased with increasing n, as shown by data 4. I_D can be regarded as the threshold fluence for the D component.

Since the A component is eliminated at the lowest laser fluence, we suggest that it is due to elimination of an adatom-type defect, i.e. a defect which, after the emission of Ga atom, leaves either the perfect configuration or another defect configuration with a higher stability against laser irradiation emerges. In this case, $N_D(0) = Y_0/\alpha$ and hence $\alpha/\eta = 1$. If $\alpha/\eta = 1$ holds for the S component, $N_D(0)$ for the S component is higher than for the A component. Alternatively, if we consider that $\alpha/\eta < 1$ for the S component, the defect concentrations of the S component can be the same and even less than those for the A component. $\alpha/\eta < 1$ may result if particle emission arises from the kink sites of steps; removal of an atom transfers the defect site to the nearest-neighbour site, keeping the structure of defects unchanged until another type of defect emerges. We are tempted to take the latter alternative and refer to the defect that gives rise to the S component as a step-type defect which, after the emission of a Ga atom, leaves a site which has nearly the same stability as before the emission. If the particle emission is initiated from a vacancy cluster, neighbouring sites are destroyed and hence the size of the cluster increases as irradiation proceeds. Therefore the D component can be ascribed to vacancy-initiated particle emission, although the possibility that the D component arises from defect-free sites cannot be excluded.

We did not measure the ejection of P atoms, for which no dye laser for RIS is available at present. No other technique can detect the emission of P atoms with the sensitivity at which Ga atoms are detected. Since the yield continues to decrease, we presume that the stoichiometry is maintained on the surface to a certain degree, and hence that ejection of either Ga or P atoms, whichever is strongly bonded, will be the rate-determining process.† We expect that nearly the same amounts of Ga and P atoms are ejected by a laser pulse and no substantial difference should exist whether measurements of Ga or P atoms are carried out.

Defect-initiated ejection of atoms is induced if the interaction of electrons and holes with defects causes substantial bond weakening or causes asymmetrical lattice relaxation, leading eventually to atomic ejection [9]. Local lattice relaxation around defects by trapping an electron and/or hole in the bulk of solids is well known [10]. Because of the superlinear dependence of the emission yield on the laser fluence, we should assume that at least two excitation events are needed for particle emission. Therefore we suggest that localization of two electron–hole pairs at defect sites causes Ga^0 emission. The occupation of two holes weakens the binding of the emitted atom, and the electronic excitation energy possessed by two electron–hole pairs is converted to the lattice energy needed for the emission of the atom. The process of two-hole localization can be regarded as a negative-U interaction, in which two holes can be localized at a defect site when $(U - E_{LR}) < 0$, where U is the on-site hole Coulomb repulsion energy and E_{LR} is the lattice relaxation energy [11]. The superlinear relation between emission yield and laser fluence has been explained in terms of the screening of Coulomb repulsion [12] and of the degeneracy of the electron–hole plasma [13]. In each case a larger laser fluence is needed to emit atoms from the defect sites for which the negative-U attractive potential is smaller.

† If the stoichiometry is changed, the yield is considered to increase as is the case above the threshold.

Table 1. A Born–Haber cycle describing the two-hole mechanism of Ga^0 neutral emission: PL, perfect lattice. $2E_{gap} + U - 2E_t - E_{LR} - E_{vap} = 0$.

PL → 2e + 2h	$2E_{gap}$
Defect + 2h → $(\text{defect})_{2h}$	$U - 2E_t$
$(\text{Defect})_{2h}$ + 2e → Ga^0(vacuum) + $(\text{defect})_{\text{missing } Ga^0}$	$-E_{LR}$
Ga^0(vacuum) + $(\text{defect})_{\text{missing } Ga^0}$ → PL + defect	$-E_{vap}$

According to the results in figure 2, larger laser fluences are needed to emit particles initiated by defects in the order of A, S and D types, while we presume that the emitted Ga^0 atom is bonded more strongly in this order [14]. In order to correlate the threshold laser fluence or E_{LR} with the bonding strength or vaporization energy E_{vap}, we used a Born–Haber cycle shown in table 1. Firstly, two electron–hole pairs are produced from the perfect lattice site on the surface by putting twice the surface gap energy, i.e. $2E_{gap}$, equal to the energy difference between the occupied and unoccupied surface states. Secondly, two holes are localized at a defect site; U is needed for putting two holes on the same site and twice the trapping energy, i.e. $2E_t$, is emitted. The electron may be loosely bound by two localized holes. Thirdly, the two-hole and two-electron localized state described above relaxes by ejecting Ga^0, leaving the defect with a missing Ga^0; here E_{LR} is gained. By putting a Ga^0 atom back on the defect with the missing Ga^0, the initial perfect lattice with the defect is gained at a cost of E_{vap}. Since the total energy for the cycle is zero, we obtain

$$U - E_{LR} = E_{vap} - 2E_{el} \tag{1}$$

where $E_{el} = E_{gap} - E_t$ is the electronic excitation energy at the defect site. E_{vap} is approximately the difference between zE_{coh} and the relaxation energy after vaporization, where E_{coh} is the cohesive energy per bond and z the number of bonds. Since E_{coh} is about 1.7 eV [15], we expect that the value of $U - E_{LR}$ can be negative. For most strongly bonded atoms, E_{vap} is larger and hence E_{LR} is smaller. This may explain the experimental results that a higher laser fluence is needed to emit atoms from adatoms, steps and vacancies in increasing order.

In conclusion, we showed that defect-initiated particle emission from the GaP(110) surface is indeed observed for laser pulses of subgap photon energies. The results can give information on extremely low concentrations on the GaP(110) surface. At least two types of defect have been distinguished by observing the variation in Ga^0 yield as a function of repeating laser pulses of subgap energies: A type or adatom type and S type or step type. We observed also a very sharp threshold laser fluence for damage evolution, which may be ascribed to vacancy-initiated particle emission. The difference in the threshold laser fluence for ejection of defects of each type and the dependence of the yield on the number of shots are shown to be utilized for characterizing surface defects as low as 10^{-5} in concentration.

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