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Electronic processes in laser-induced Ga^0 emission and laser ablation of the GaP(110) and GaAs(110) surfaces

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Abstract. We have carried out sub-monolayer sensitivity measurements of laser-induced Ga^0 emission from the GaP(110) and GaAs(110) surfaces using a resonant ionization technique. The laser ablation threshold fluence is defined as the critical fluence above which an increase of the Ga^0 emission yield is observed by repeated irradiation with laser pulses on the same spot but below which a decrease of the yield is observed. The photon-energy dependences of the laser ablation threshold fluence and the sub-ablation emission yield have been investigated for photons below, near and above the bulk band-gap energies in both GaP and GaAs. For photons below the band-gap energies, the sub-ablation emission and laser ablation are observed and ascribed to photon absorption by defects on the surfaces. The sub-ablation emission is found to be reduced substantially at a photon energy slightly below the band-gap energies for both GaP and GaAs; the reduction is of resonance type for GaAs and stepwise for GaP. Only a small amount of emission is observed for GaP for photons above the band-gap energy. The ablation threshold fluence for GaAs shows a resonant-type increase, corresponding to the resonance-type reduction of the sub-ablation emission yield, while the ablation threshold fluence for GaP does not change on crossing the band-gap energy. For photons above the band-gap energies, the ablation threshold fluence decreases with increasing photon energy in a similar manner for both GaP and GaAs. The decrease in the ablation threshold fluence for the GaAs(110) surface appears to be correlated to the increase in the sub-ablation emission yield as observed previously. These results of the photon energy dependence of the sub-ablation emission yield and ablation threshold fluence are explained in terms of the electronic excitation of defects on surfaces and of surface occupied states.

1. Introduction

Laser ablation, the removal of material from a solid surface by laser irradiation, observed for non-metallic materials such as semiconductors [1–3], insulators [4, 5] and polymers [6–8] is rapidly becoming a subject of both scientific interest in surface physics and photochemistry and technical interest for application such as laser-induced etching and deposition of thin films including superconductors [9–11]. It has been established that the ablation process depends on the wavelength, fluence and pulse width of laser beams. Basically two mechanisms for laser ablation of materials have been suggested: electronic [12] and thermal [13]. The former emphasizes that electronic processes play an important role, though a temperature rise may occur simultaneously and make an additional contribution to ablation. The latter assumes that the damage of the surface occurs as a result of melting due to local heating, though photons are absorbed primarily through electronic transitions. Despite a number of attempts at understanding the basic mechanism, the origin of laser ablation is still controversial. One of the reasons is that, as demonstrated for metals [14], the

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rapid rise of surface temperature during pulsed laser irradiation makes it almost impossible to differentiate between the contribution of the initial electronic process to laser ablation, if any, and that of the laser-induced heating. An important key to revealing the initial electronic process is to use a cleaned surface and then measure the emission yield at high sensitivity under conditions where the surface damage is negligible.

High sensitivity measurements of the emission of Ga^0 atoms from the GaP(110) and GaAs(110) surfaces by pulsed laser irradiation have revealed that Ga^0 emission is induced by photons of sub-band-gap energies [15–18]. In these measurements atoms of 10^{-6} monolayer emitted by a single laser pulse have been detected. The process is non-thermal, because the optical absorption coefficient for photons in this energy region is too low to heat the sample. Two-photon absorption as a cause of such emission has been excluded because of the low cross section [15, 16].

Based on the results of high-sensitivity measurements [15], which show that the emission yield Y induced by a laser pulse changes as the number n of pulses incident on the same spot on the surface increases, the emission is attributed to originate from defects on the surface by breaking the bonds of weakly bonded atoms (WBAs) forming defects. The Y–n relation exhibits first a rapid decrease and then a slow decrease when the fluence is low, while it exhibits an increase when the fluence is high. The rapid decrease in the emission yield is regarded as originating from adatoms, of which removal leaves a perfect surface. The slowly decreasing component is attributed to the emission from kinks on steps, for which the emission of an atom leaves a new kink site of a similar structure [16]. The rapidly decreasing component is called the A component and slowly decreasing component the S component. In addition, there are vacancy-type defects on surfaces, and the removal of WBAs around a vacancy on the surface produces a vacancy cluster with more WBAs. Thus when the emission originates from vacancies, the yield is expected to increase, as is indeed observed at high fluences. In order to emphasize the difference between the contributions to the emission of the adatoms and steps and of vacancies, we tentatively refer to the former as on-surface-type defects, located above the surface, and the latter as sub-surface-type defects, located below the surface.

It has been also pointed out [16] that there exists a distinct threshold fluence between that inducing an increasing Y–n relation and that inducing a decreasing Y–n relation. We designate this fluence as F_{th}. It has also been shown that Y depends on laser fluence F very strongly in the range where an increasing Y–n relation is observed; often described as a power function of F^{10-15}. Thus as the fluence increases beyond F_{th}, the emission yield increases rapidly and a massive emission of atoms will result even at fluences slightly higher than F_{th}. It has been shown that the photon-energy dependence of F_{th} for both GaP and GaAs is parallel to that of the laser ablation threshold fluence determined from the onset of the laser-induced surface damage detected with an optical microscope [19], in the photon-energy range where F_{th} changes by a factor of five. Thus we call F_{th} the ablation laser fluence (ALF). Since F_{th} is determined by a small number of emitted atoms, its study is suitable for investigating the primary process of laser ablation. We will call the emission observed below ALF sub-ablation emission, and deal with both the sub-ablation emission and ALF in this paper.

An important feature of the defect-initiated Ga^0 emission is the super-linear dependence of the yield on laser fluence, which is observed even in the sub-ablation emission. The Y–F relation for the sub-ablation emission induced by irradiation of the GaP(110) surface with photons below the band-gap energy can be expressed as power functions F^m [16], with $m = 2$–3 for the A component and $m = 4$–6 for the S component. These power indices are ascribed to the number of excitations required to induce the emission of WBAs associated with each defect. The larger power index above ALF, $m \sim 15$, is partly attributed to the increase in the number of WBAs during a laser pulse [20]. The non-linear Y–F relations suggest that the mechanism of the laser-induced atomic emission from semiconductor surfaces is completely different from the MGR (Menzel, Gomer and Readhead) mechanism [21, 22], which results in a linear Y–F relation.

The spectroscopic studies of the sub-ablation emission yield and ALF provide further evidence that both processes are electronic. As reported for the GaP(110) [23] and GaAs(110) [18] surfaces, the yield of sub-ablation emission is substantially reduced when the photon energy crosses the band-gap energy. This rules out totally the possibility of Ga^0 sub-ablation emission being induced by heating of surface layers due to bulk optical absorption. Furthermore Ga^0 sub-ablation emission yield is enhanced at certain photon energies corresponding to the energies of electronic transitions involving intrinsic surface states for GaAs(110) [24], suggesting that two-dimensional electron–hole pairs (2D e–h pairs) produced in the relaxed surface state are more effective in sub-ablation emission. ALF for the GaP(110) surface does not change even if the photon energy crosses the band-gap energy, suggesting that the onset of the bulk optical absorption, which is the main heating source, does not influence the ablation process of GaP.

In order to understand further the mechanism of sub-ablation emission and laser ablation, it is desirable to carry out systematic investigations of their photon-energy dependences for GaP and GaAs. Many III–V compound semiconductor crystals have the zinc blende structure and their (110) surfaces relax in such a way that the group-III atoms move inwards and the group-V atoms move outwards. Because of this atomic relaxation, the surface electronic states, originating from the dangling bonds and separated into the lower occupied and higher unoccupied states, are removed from the fundamental gap. Although GaP was believed to be an exception in that the surface unoccupied state lay in the fundamental gap [25–31], recent photoemission experiments by Chiaradia *et al* [32] have suggested that practically there is no intrinsic surface unoccupied state below the edge of the conduction band. The accurate energy position of the unoccupied state of the GaP(110) surface is still controversial.

In view of the available limited wavelength range of dye lasers, the GaP(110) surface is particularly suitable for investigating the photon-energy dependence for sub-gap and above-gap photo-excitations. Excitations by photons below and above the band-gap energy are expected to induce different defect excited states: localized defect excited states or resonant states interacting with the continuum. Delocalized 2D and 3D e–h pairs are also produced by photons above the band-gap energy. It is to be noted that the bulk optical absorption coefficients of GaP and GaAs exhibit different photon-energy dependence: GaP and GaAs are indirect and direct semiconductors, respectively.

The purpose of this paper is to reveal the correlation between laser ablation and sub-ablation emission by investigating their photon-energy dependences in detail. We have clarified the photon-energy dependences of the sub-ablation emission yield and the ALF near and above the band-gap energies for GaP(110) and GaAs(110) surfaces. We have shown that ALFs for both of these surfaces are reduced, in a similar way as the photon energy increases above the bulk band-gap energy. The correlation between the laser ablation and the sub-ablation emission below, near and above the band-gap energies is discussed in detail.

2. Experimental

The experimental technique used in the present study is basically the same as published elsewhere [16]. The (110) sample surfaces, polished mechanically and then etched chemically in a solution of HCl : HNO_3 : H_2O = 2 : 1 : 1 at 55 °C for GaP (n type, S doped) and H_2SO_4 : H_2O_2 : H_2O = 3 : 1 : 1 at 60 °C for GaAs (n type Si doped), were placed in an ultra-high vacuum (UHV) chamber, in which emission of Ga^0 atoms induced by laser irradiation was measured using the resonant ionization technique. The surface was cleaned by Ar^+ ion sputtering (500 eV) and subsequent annealing for several minutes at 550–600 °C for GaP and at 500–550 °C for GaAs. After these procedures the (110) surface was monitored by low energy electron diffraction (LEED) and Auger electron spectroscopy (AES); clear (1 × 1) LEED patterns were found and no contamination above a detection limit of AES was detected on the surface before laser irradiation.

The sample temperature was changed by changing the electric current through a W wire attached to the back of a sample holder. The temperature was monitored by a chromel–alumel thermocouple attached to the sample holder. The heat flow from the sample holder system was kept so small that the temperature difference between the sample itself and the sample holder was less than 20 K.

Ga^0 sub-ablation emission and ablation were induced by a 28 ns pulsed laser beam generated with an excimer-pumped dye laser (Lamda Physik, EMG203MSC and FL3002), which was incident on the surface with an angle of 45°. In order to obtain the beam profile incident on the surface of the sample, a beam reflected by a mirror in the optical path to the sample was guided to a position equivalent to the sample surface, where the beam was shadowed partially by a movable knife edge and the transmitting beam fluence was measured with a calorimeter. The beam size estimated by taking the width at $1/e$ points of the peak fluence was typically 200 μm for both horizontal and vertical directions. By measuring the beam profile every time the laser wavelength was changed, it was possible to compare the fluences for different wavelengths with an accuracy of 15%.

The emitted Ga^0 atoms were resonantly ionized by a laser beam from another excimer-pumped dye laser system incident parallel to the surface of the sample. The ionized atoms were collected to a microchannel plate: the detection system was equipped with a time-of-flight capability that could detect ionized Ga^0 atoms separately from other impurity ions such as alkali-metal ions. The Ga^+ ion signal was found to be extremely small for laser fluence below and near ALF. The present technique allows the detection of only Ga^0 atoms, but we expect that P or As atoms of almost the same number as Ga^0 atoms are emitted. The sensitivity of the detection system was high enough that 10^{-6} monolayer atoms emitted by a single laser pulse can be detected. The sensitivity was determined by measuring the intensity of the signal of Ga^0 atoms emitted from an Si surface on which a given amount of Ga^0 atoms were deposited. The base pressure throughout the measurements of laser-induced emission was less than 2×10^{-8} Pa.

The sub-ablation emission yield obtained for several photon energies for the GaP(110) and GaAs(110) surfaces have been shown to be scaled by $\varepsilon = h\nu - E_G(T)$ [23,24], where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at the sample temperature T. Thus in obtaining the photon-energy dependences of the ALF and sub-ablation emission yield, we changed both the laser wavelength and sample temperature. The former is employed mainly for scanning the photon energy over a wide range and the latter for scanning ε in a narrow range. Though changing the wavelength of a dye-laser system alters the beam-fluence profile, changing the temperature does not: the ε scan by the latter method yields a more exact ε dependence of ALF and sub-ablation emission yield. The temperature was scanned from 300 K to 700 K. A 100 K scan of the temperature corresponds to about a 50 meV [33] scan of photon energy for GaP and GaAs.

3. Experimental results

3.1. Fluence dependence of the Ga^0 emission yield below and above ablation laser fluence

As pointed out in the introduction, the emission yield of Ga^0 atoms changes both for GaP and for GaAs as the irradiation at the same spot is repeated. Figure 1 shows a typical Y–n relation obtained with photons of 2.07 eV for the GaP(110) surface. The rapidly decreasing component (A component) and the slowly decreasing component (S component) are observed at 1.0 J cm^{-2}, while the yield increases as the shot number increases at 1.3 J cm^{-2}. According to this result, the ALF lies between 1.0 J cm^{-2} and 1.3 J cm^{-2}. In practice, however, we determined the ALF by measuring the Y–F relation between yield Y and laser fluence F as explained later.

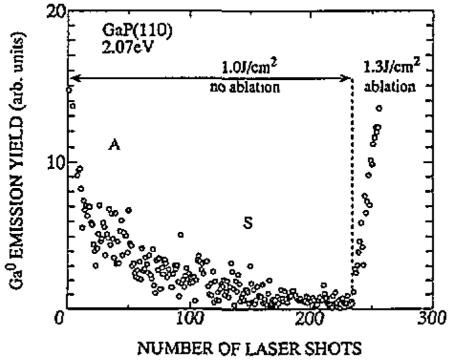

Figure 1. The shot number dependence of Ga^0 emission yield for repeated irradiation on the same spot of the GaP(110) surface for laser fluences of 1.0 J cm^{-2} and 1.3 J cm^{-2} and photons of 2.07 eV.

Figure 2 shows the Y–F relations for fluences below and above ALF for the GaP(110) surface and figure 3 shows those for the GaAs(110) surface. Both figures show the Y–F relations for photons (a) below, (b) near and (c) above the bulk band-gap energies. The ε value is shown in each figure and is used as an energy scaling factor. $E_G(T)$ is obtained using the empirical formula given by Panish and Casey [35] as $E_G(T)$ (in eV) $= 2.338 - 6.3 \times 10^{-4}\ T^2/(T + 460)$ for GaP and $E_G(T)$ (in eV) $= 1.522 - 5.8 \times 10^{-4}\ T^2/(T + 300)$ for GaAs. The emission yield is found to be a superlinear function of F for all cases, and each Y–F relation can be fitted by a power function as shown on the log–log plot in the lower panel of each figure. All data were taken at room temperature (297 K) except figure 3(b), for which 350 K was employed. In the figures, open circles denote the Y–F relation obtained for a fresh spot, while full triangles and squares are those obtained after the A component is eliminated by repeated irradiation. Squares denote the data points for the fluences where the increasing Y–n relation was observed. Thus, for photons below the band-gap energies for both GaP and GaAs (figures 2(a) and 3(a)), the open circles denote the Y–F relation for the A component and the full triangles denote that for the S component, while the squares denote the Y–F relation leading to ablation. The power indices above ALF are larger than 10 and much higher than those for the A and S components. We determined ALF as a fluence that gives a yield of three units in the Y–F relation showing a power index larger than 10. According to these figures, ALF for the GaP(110) surface was found to be 1.15 J cm^{-2} and that for GaAs(110) to be 400 mJ cm^{-2}.

The Y–F relations for photons near the band-gap energies (figures 2(b) and 3(b)) are substantially different from those for photons below the band-gap energies. The difference is clearer in the result for GaP (figure 2(b)): the yield for a fresh spot on the surface does

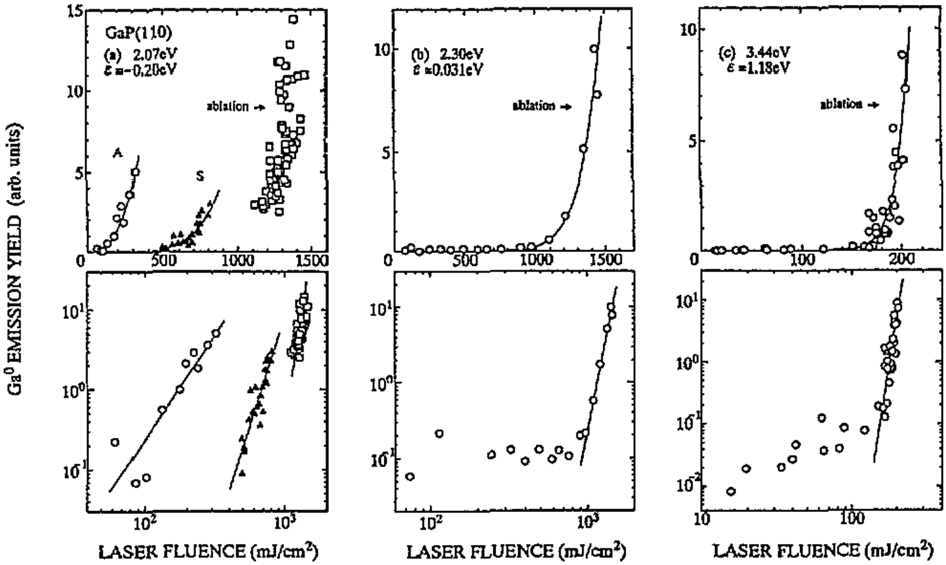

Figure 2. The laser fluence dependence of Ga^0 emission yield for GaP(110) at room temperature (297 K) for three different photon energies of (a) 2.07 eV, (b) 2.30 eV and (c) 3.44 eV. The values of ε defined as $\varepsilon = h\nu - E_G(T)$ are also shown within the figure, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T, obtained from [33]. The emission yields are plotted on a linear scale in the upper panel and on a logarithmic scale in the lower panel for each photon energy. The power indices obtained from the log–log plots of (a) are 2.6, 5.4 and 11.2 for the A and S components and laser ablation, respectively, that of (b) is 10.0 for laser ablation and that of (c) is 15.0 for laser ablation.

not increase abruptly until the fluence crosses 1.1 J cm^{-2}. The Y–F relation in this fluence range shows a power dependence with a power index of 10. We determined the ALF to be 1.3 J cm^{-2} from this figure. Only a small amount of emission, of the order of the noise level and not very dependent on fluence, is observed below ALF. A similar difference is observed for GaAs (figure 3(b)) as well: a rapid increase in the yield is observed only for laser fluence above 500 mJ cm^{-2}. Similarly as for GaP, we determined the ALF for GaAs to be 540 J cm^{-2} from figure 3 (b). These results indicate that the Y–F relations characteristic of the A and S components are absent at $\varepsilon = 0.031$ eV for GaP and at $\varepsilon = -0.035$ eV for GaAs.

For photons above the band-gap energies (figures 2(c) and 3(c)), a difference in sub-ablation emission of the GaP(110) and GaAs(110) surfaces is evident: the A and S components are observed for GaAs but absent for GaP. It is also clear that the ALF is much smaller in this case than those for photon energies below the band-gap energies for both GaP and GaAs. Further details of the ε dependences of the sub-ablation emission yield and ALF for the GaP(110) and GaAs(110) surfaces are described in the following sections.

3.2. Temperature dependences of ablation laser fluence and sub-ablation Ga^0 emission yield for sub-band-gap photons

We have investigated the temperature dependence of sub-ablation emission yield and ALF for the GaP(110) surface in the photon energy range between 1.35 eV and 2.00 eV, where only direct defect excitation is the cause of the sub-ablation emission and laser ablation. Figure 4 shows the temperature dependence of the sub-ablation emission yield for several

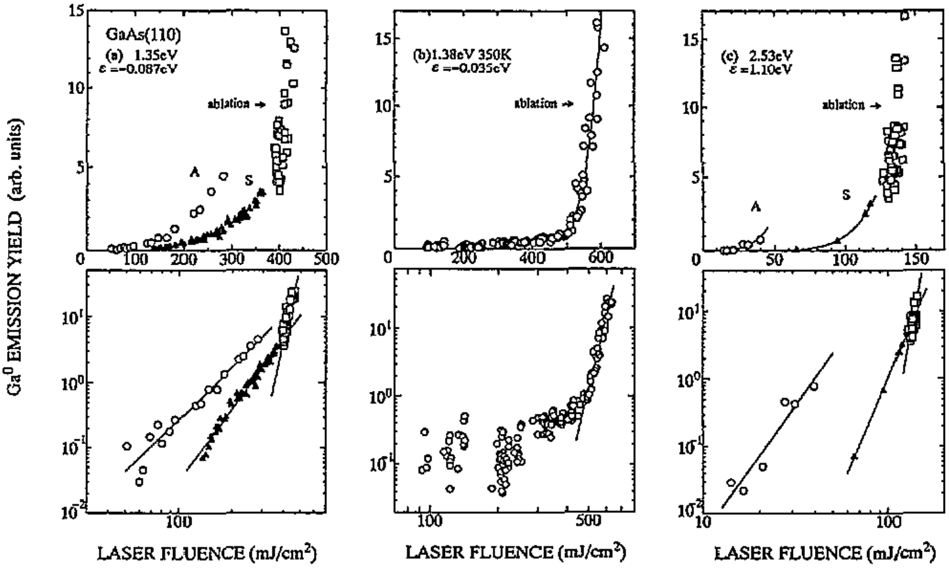

Figure 3. The laser fluence dependence of Ga^0 emission yield for GaAs(110) for three different values of ε: (a) $\varepsilon = -0.087$ eV; (b) $\varepsilon = -0.035$ eV and (c) $\varepsilon = 1.10$ eV. ε is defined as $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T, obtained from [33]. These values of ε were obtained for photons of (a) 1.35 eV and (c) 2.53 eV at room temperature (297 K) and for photons of (b) 1.38 eV at 350 K. The emission yields are plotted on a linear scale in the upper panels and on a logarithmic scale in the lower panels. The power indices obtained from the log–log plots of (a) are 2.6, 3.6 and 11.4 for the A and S component and laser ablation, respectively, that of (b) is 14.1 for laser ablation and those of (c) are 3.8, 6.4 and 15.2 for the A and S components and laser ablation, respectively.

sub-band-gap photon energies. The data points in the figure include the results of the temperature dependence of the S-component yield obtained at several spots on the surface for several photon energies; the plots of the same symbol showing different yield at a given temperature were obtained at different spots. The overall temperature dependence is found to be very weak, although the results show an unsystematic distribution of data points beyond the experimental error. Such a distribution seems to arise from the difference in the temperature dependence of the optical absorption coefficient of a specific defect state involving the emission of Ga^0 by photons of a given energy.

Figure 5 shows the temperature dependence of ALF for a photon energy of 1.70 eV. Two different positions on a sample were taken to obtain ALF at each temperature. Since the ALF depends on the location of an irradiated spot, we can only conclude from the experimental results of figure 5 that the ALF decreases slightly as the temperature increases or is almost independent of temperature.

3.3. Photon energy dependences of ablation laser fluence and sub-ablation Ga^0 emission yield

3.3.1. Near the band-gap energy. In this section we describe the photon-energy dependences of sub-ablation emission yield and ALF for the GaP(110) and GaAs(110) surfaces at photon energies near the band-gap energies. A detailed photon-energy dependence of the sub-ablation emission yield and ALF for a short range scan around the band-gap energy ($\varepsilon \simeq 0$) is obtained by changing the sample temperature.

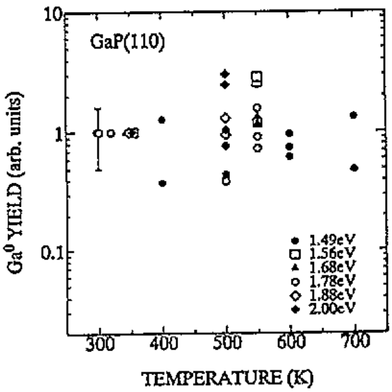

Figure 4. The temperature dependence of Ga^0 sub-ablation emission yield for several photon energies below the band-gap energy for the GaP(110) surface. The yield obtained with laser beams of several photon energies between 300 K and 350 K were taken to be unity. An error bar is shown only for the data point at 300 K but is nearly the same for other data points.

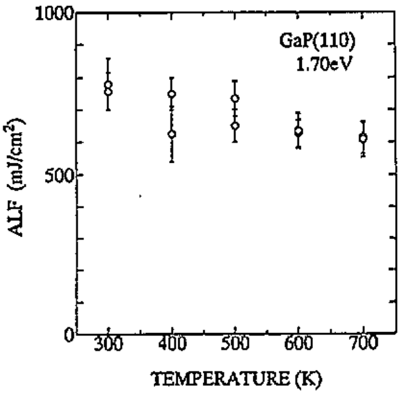

Figure 5. The temperature dependence of ablation laser fluence (ALF) for photons of 1.70 eV for GaP(110).

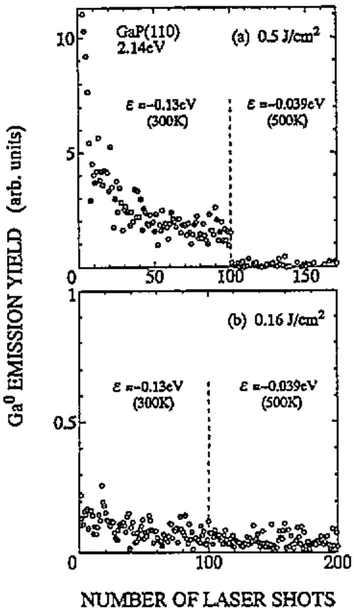

Figure 6. The shot number dependence of Ga^0 sub-ablation emission yield for two slightly different values of ε, $\varepsilon = -0.13$ eV and -0.039 eV, for laser fluences of (a) 0.5 J cm^{-2} and (b) 0.16 J cm^{-2} for photons slightly below the band-gap energy (2.14 eV) for GaP(110). ε is defined as $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T, obtained from [33]. The sample temperature was changed from 300 K to 500 K for fixed photon energy to change the value of ε.

Figure 6 shows the Y–n relation for the sub-ablation emission at a photon energy of 2.14 eV and laser fluence of (a) 0.5 J cm^{-2} and (b) 0.16 J cm^{-2}. The value of ε was altered at $n = 100$ by changing the temperature from 300 K to 500 K. Figure 6(a) shows that the emission yield, after it becomes nearly constant after repeated irradiation, decreases substantially when ε is increased. No similar substantial reduction in the emission yield, however, is observed when laser pulses of the lower fluence are employed. This residual emission is of the same nature as those shown in figure 2(b) and (c).

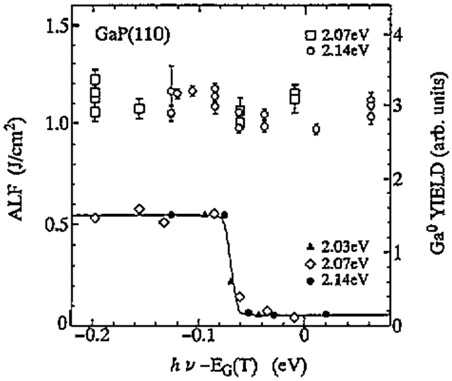

Figure 7. Ablation laser fluence (ALF) and Ga^0 sub-ablation emission yield for photons slightly below the band-gap energies for GaP(110) as a function of $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the band-gap energy at temperature T. $E_G(T)$ for GaP is obtained using the empirical formula, $E_G(T) = 2.338 - 6.3 \times 10^{-4}\ T^2/(T + 460)$, from [33]. These ε dependences were obtained by changing the sample temperature between 300 K and 700 K for photons of 2.07 eV (open squares) and 2.14 eV (open circles) for ALF and those of 2.03 eV (full triangles), 2.07 eV (open diamonds) and 2.14 eV (full circles) for the sub-ablation emission yield. The laser fluences for inducing the sub-ablation emission were about half the ALF at 300 K for each photon energy. The sub-ablation emission is substantially reduced around $\varepsilon = -70$ meV, as indicated by a solid line.

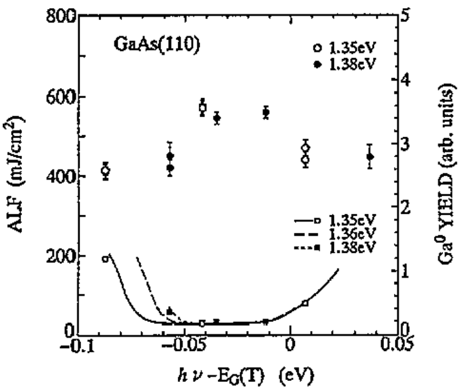

Figure 8. Ablation laser fluence (ALF) and Ga^0 sub-ablation emission for GaAs(110) for photons near the band-gap energy as a function of $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T. $E_G(T)$ for GaAs is obtained using the empirical formula, $E_G(T) = 1.522 - 5.8 \times 10^{-4}\ T^2/(T + 300)$, from [33]. These ε dependences were obtained by changing the sample temperature between 300 K and 500 K for photons of 1.35 eV (open circles) and 1.38 eV (full circles) for ALF and for photons of 1.35 eV (open squares) and 1.38 eV (full squares and short-dashed line) for the sub-ablation emission yield. The solid line and long-dashed line indicate ε dependences of sub-ablation emission yield for photons of 1.35 eV and 1.36 eV, respectively, obtained from [18].

Figure 7 shows the sub-ablation emission yield of the S component for photons of energies of 2.03, 2.07 and 2.14 eV and also the ALF for photons of energies of 2.07 eV and 2.14 eV, plotted as a function of ε for GaP(110), obtained by varying the temperature.

As shown by the solid line, sub-ablation emission yield is substantially reduced around $\varepsilon = -70$ meV. On the other hand, the ALF depends little on ε: i.e. the crossing of the photon energy over the band-gap energy does not influence the ALF.

A similar ε dependence of sub-ablation emission yield for photons of 1.35, 1.36 and 1.38 eV and that of ALF for photons of 1.35 eV and 1.38 eV for GaAs(110) are shown in figure 8; the results for the sub-ablation emission for 1.35 eV (solid line) and 1.36 eV (dashed line) have been published elsewhere [18]. Open squares and full squares with a dotted line are the results of the ε dependence of the sub-ablation emission yield for photons of 1.35 eV and 1.38 eV, respectively, obtained with the same sample as used to obtain the ε dependence of ALF. The sub-ablation emission yield is substantially reduced in the range from $\varepsilon = -50$ meV to $\varepsilon = -70$ meV, depending slightly on the photon energies of the laser pulse, and recovered near $\varepsilon = 0$. The difference in the ε dependence of the sub-ablation emission yield observed in GaAs and GaP can be attributed to the difference in their bulk band structures, which is direct for GaAs and indirect for GaP, as will be discussed later. The ALF obtained for photons of 1.35 eV (open circles) and 1.38 eV (full circles) shows a little ε dependence: the ALF between $\varepsilon = -45$ meV and $\varepsilon = -10$ meV is about 40% higher than those at higher and lower ε. This seems to be correlated to the reduction of sub-ablation emission yield in the same ε range for GaAs(110).

3.3.2. Above the band-gap energy. We measured the ALF as a function of ε for the GaP(110) and GaAs(110) surfaces and the sub-ablation emission yield for GaP(110) for $\varepsilon > 0$. Figures 9 and 10 show the ε dependences of (a) ALF and (b) sub-ablation emission yield for GaP and GaAs, respectively. Figure 10(b) is reproduced from the ε dependence of the sub-ablation emission yield for the GaAs(110) surface reported by Kanasaki *et al* [18].

In figures 9(a) and 10(a), open circles indicate the ε dependence of ALF obtained by changing the wavelength of laser pulses at 300 K and open squares indicate a similar ε dependence obtained at 500 K. Data obtained at 400 K are also plotted at $\varepsilon = -10$ meV and $\varepsilon = -40$ meV for GaAs(110). Solid lines in figures 9(a) and 10(a) indicate the bulk optical absorption coefficient α of GaP [34, 35] and GaAs [36, 37], respectively. The ε dependences of ALF for both GaAs and GaP are similar: they start to decrease at $\varepsilon = 0.2$–0.3 eV and decrease further at $\varepsilon = 0.8$–1.1 eV.

Data points in figure 9(b) are obtained by changing the temperature for several photon energies. The sub-ablation emission yield is extremely small in GaP for $\varepsilon > 0$. For the GaAs(110) surface, a correlation is found between the ε dependence of ALF and that of the sub-ablation emission yield: the former shows stepwise reductions in the energy range $\varepsilon = 0.2$–0.7 eV and 1.1–1.5 eV, while the latter increases in nearly the same energy range $\varepsilon = 0.4$–0.7 eV and 1.1–1.2 eV. A similar correlation cannot be obtained for GaP(110), in which the sub-ablation emission yield is reduced at $\varepsilon = -70$ meV and does not recover as it does in the case of GaAs.

4. Discussion

As described in section 1, the sub-ablation emission originates from on-surface-type defects (adatoms and steps), while the emission near the ALF originates from sub-surface-type defects (vacancies). We will first discuss the general feature of the Y–F and Y–ε relations for these two types of defect, which are listed in table 1.

Evidently the power indices for the Y–F relation for sub-surface-type defects for GaP and GaAs in a wide photon-energy range are larger than those for on-surface-type defects.

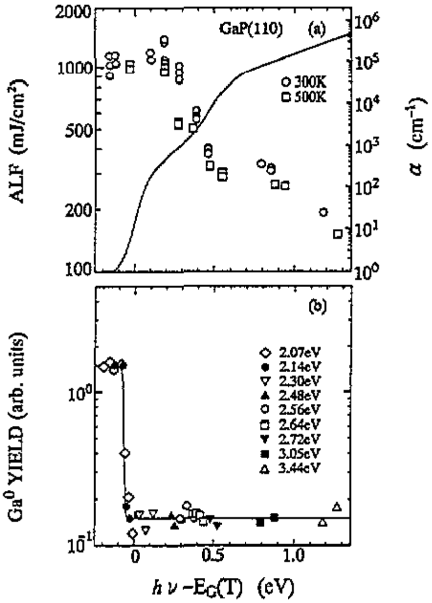

Figure 9. (a) Ablation laser fluence (ALF) and (b) Ga^0 sub-ablation emission yield for GaP(110) as a function of $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T, obtained from [33]. A solid line indicates the bulk optical absorption coefficient (α) of GaP, obtained from [34] and [35]. The ε dependence of ALF was obtained by changing the laser wavelength at 300 K (open circles) and 500 K (open squares). The data plots for sub-ablation emission yield are compiled from the results of ε dependences of Ga^0 sub-ablation emission yield obtained by changing temperature between 300 K and 500 K for several fixed photon energies in the range of 2.07–3.44 eV. A solid line shows that the sub-ablation emission yield is substantially reduced around $\varepsilon = -70$ meV and is not recovered.

The results are consistent with the suggestion that the laser ablation is initiated by vacancies on the surface; the emission of WBAs associated with vacancies on the surface leads to evolution of vacancy clusters and hence increases the number of WBAs [16]. Thus the Y–F relation involves the contributions of the bond breaking and of the increase in the number of WBAs during a laser pulse. It has been shown that the latter contribution gives a quadratic relation, and that the overall F dependence is given by $Y \propto (F^{m'})^2$, where m' is the power index required to break a WBA bond [20]. Thus although the power indices for the emission above ALF are higher than those for the sub-ablation emission, it appears that the number of excitations for breaking the bonds for WBAs on vacancies or sub-surface-type defects lies in a range of five to seven, and similarly for the on-surface-type defects. According to the present results, the power indices responsible for breaking the bonds are in the range two to seven for all defect types in GaAs and GaP.

Both sub-surface-type and on-surface-type defects can contribute to the emission induced by photons below the band-gap energies, due to the multiple electronic excitation of defects leading to bond breaking [16]. The reduction of the sub-ablation emission yield is observed slightly below the bulk band-gap energies for GaP and GaAs; stepwise for GaP and resonant type for GaAs. The increase of ALF, which corresponds to the decrease in the sub-ablation emission yield, has been observed only for GaAs and not for GaP. The photon-energy dependences of ALF above the band-gap energy for GaP and GaAs are very similar.

Sub-ablation emission and ablation induced by sub-band-gap photon energies, can only

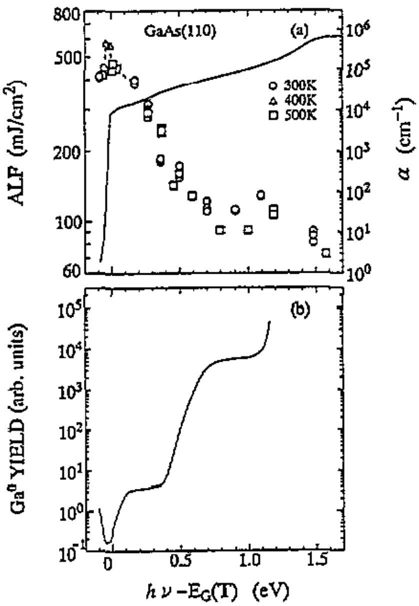

Figure 10. (a) Ablation laser fluence (ALF) and (b) Ga^0 sub-ablation emission yield for GaAs(110) as a function of $\varepsilon = h\nu - E_G(T)$, where $h\nu$ is the photon energy and $E_G(T)$ is the bulk band-gap energy at temperature T, obtained from [33]. A solid line indicates the bulk optical absorption coefficient (α) of GaAs, obtained from [36] and [37]. The ε dependence of ALF was obtained by changing the laser wavelength at 300 K (open circles), 400 K (open triangles) and 500 K (open squares). (b) is reproduced from [18].

be ascribed to photon absorption by defects. The temperature dependence of the sub-ablation emission yield and ALF for photons below the band-gap energy may involve both the cross section for optical excitation of the defects and the efficiency of atomic ejection at the excited state. The fact that there is little temperature dependence for several photon energies suggests that the temperature dependence of the cross section is small and also that the optical absorption band due to defect transitions is broad. Such a broad optical absorption band is characteristic of defects that involve strong electron–lattice coupling [38].

Formation of a resonance excited state in which a defect excited state interacts with an exciton state is considered to induce the transfer of the defect excitation energy to the bulk, reducing the sub-ablation emission yield. Another way of interpreting the cause of the reduction of the yield is the resonance energy transfer from the defect excited state to the bulk exciton. From the point of view of the multiple excitation model, such an energy transfer to the bulk that occurs at any stage of a series of multiple excitations will prohibit the emission. In order that the sub-ablation emission yield is reduced, such a transfer should occur before the start of relaxation of the defect excited state leading to the emission. We presume that such a rapid transfer of the defect excitation energy to the bulk is the cause of the reduction of the yield near the bulk band-gap energy.

The reduction in the yield of the sub-ablation emission near the band-gap energy is observed for the on-surface-type defects in both GaP and GaAs; stepwise in the former and resonant type in the latter. For GaAs, which is a direct semiconductor, the exciton state near the bulk band-gap energy perturbed by defects on the surface consists predominantly of the excitons at the Γ point. Thus the resonant energy transfer from the defect excited state on the surface to the bulk can occur only in the energy range of the exciton at the Γ

Table 1. Characteristics of laser-induced Ga^0 emission initiated from on-surface-type defects (adatom-type and step-type defects) and sub-surface-type defects (vacancy-type defects) observed for the (110) surfaces of GaP and GaAs.

			Photon energy dependence			
	Y–n relation	Power index m in $Y \propto F^m$	Quantity observed	Material	Near band-gap energy	Above band-gap energy
On-surface-type defect	decrease	2–7	sub-ablation emission yield	GaP	stepwise reduction	extremely small
				GaAs	resonant-type reduction	stepwise increases
Sub-surface-type defect	increase	10–15[a]	ablation laser fluence (ALF)	GaP	no change	stepwise reductions
				GaAs	resonant-type increase	stepwise reductions

[a] The number is doubled because of accumulation of WBAS.

point. On the other hand, the similar perturbed exciton state near the indirect band gap of GaP consists of excitons that have different translational momentum and hence extends to a higher energy above the indirect band gap [39]. Therefore the resonance energy transfer for GaAs is expected to be limited to the near-band-gap energy range, while that for GaP is expected to extend to higher energies. It is to be noted that these considerations suggest further that the bulk excitation does not make any contribution to the sub-ablation emission.

Another difference between GaP and GaAs is that an increase in the ALF near the band-gap energy is observed only for GaAs and not for GaP (figures 7 and 8). If the same mechanism of the resonance transfer used to account for the reduction of the sub-ablation emission yield can be applied to explain the increase in ALF, then one expects an increase in ALF near the bulk band-gap energy for both GaP and GaAs. However a resonant-type increase is observed only in GaAs. Two competing processes are conceivable for the transfer of the energy of defect excitation to the bulk: the resonant energy transfer, as described above, and the migration of the excitons away from the surface into the bulk. The former, which causes a decrease in the sub-ablation emission yield and an increase in the ALF, appears to be more favourable for the decrease in sub-ablation emission yield in GaAs and GaP and for the increase in the ALF of GaAs. The experimental result that no change in ALF is observed for GaP appears to indicate that the migration of the excitons generated by the resonant energy transfer is inhibited for sub-surface-type defects in GaP and that the exciton excitation energy is dissipated by defects.

For photon energies above the band-gap energy, we note in particular that the photon-energy dependences of ALF for GaP and GaAs are very similar: it decreases at $\varepsilon \sim 0.3$ eV and again at $\varepsilon \sim 1.0$ eV. These results are important with respect to two points of view: (a) the photon-energy dependence of the bulk optical absorption coefficient for GaP and GaAs is completely different but the those of ALF are similar; and (b) the photon-energy dependence of the sub-ablation emission yield is correlated with that of ALF for GaAs.

The bulk optical absorption coefficient changes abruptly across the bulk band-gap energy for -0.1 eV $< \varepsilon < 0.3$ eV, by three orders of magnitudes for GaP and by four orders of magnitudes for GaAs, yet there is almost no decrease in ALF in this energy range. The change in optical absorption coefficient for 0.3 eV $< \varepsilon <$ 1.0 eV for GaP is two orders of magnitude and only by a factor of five for GaAs, but ALF changes by a factor of three. Thus there is no direct correlation between the bulk optical absorption coefficient and the ALF [19].

The correlation between the photon-energy dependences of ALF and the sub-ablation emission yield for GaAs suggests that the process that enhances the sub-ablation emission yield reduces the ALF. Kanasaki *et al* [24] have suggested that the stepwise enhancements of the sub-ablation emission yield for the GaAs(110) surface occur at photon energies corresponding to the direct transitions from the surface occupied state [40] to the bulk conduction band and to unoccupied states [41] at the $\overline{\Gamma}$ point. The correlation for GaAs suggests that the decrease of the ALF can be explained in terms of the onset of the transitions involving the surface states. The transition from the occupied surface state to the unoccupied bulk state for GaP has been found to occur at $\varepsilon \sim 0.5$ eV [42]. The experimental results for the energy of transition from the occupied surface state to the unoccupied surface state for GaP are scattered and in the range of $\varepsilon = 0.2$–1.2 eV [31, 43, 44]. Therefore, it is not yet possible to draw any conclusion on the ε dependence of ALF for GaP. However, because of the similar dependences of GaP and GaAs, we suggest that the same mechanism can be used to explain the ε dependence of ALF as for GaAs.

The reduction in ALF by the initiation of the surface optical transitions suggests that the 2D e–h pairs confined within the surface states contribute to laser ablation very effectively.

The decrease in ALF at the onset of the transitions involving the surface occupied states can be attributed to the increase in the number of excitations confined to the surface. The absence of enhancement of the sub-ablation emission yield for GaP at these photon energies suggests that the escape of the excitation energy of the on-surface-type defects to the bulk excited state is particularly effective for GaP. Further detailed theoretical studies are needed to reveal the interactions between the excited states of defects on surfaces, surface excitons and bulk excitons.

5. Conclusion

In conclusion, we have investigated here the photon-energy dependences of laser-induced sub-ablation emission yield and ablation laser fluence (ALF) for the GaP(110) and GaAs(110) surfaces using the high-sensitivity measurements. The sub-ablation emission yield is found to be substantially reduced for photons slightly smaller than the band-gap energy for both the GaP(110) and GaAs(110) surfaces: the reduction is stepwise for GaP and resonant type for GaAs. For laser ablation we presented evidence that its initial process is purely electronic: we found that the photon-energy dependence of ALF for both GaP and GaAs determined by high-sensitivity measurements shows no direct correlation to that of the bulk optical absorption coefficient. Furthermore the photon energy dependence of ALF shows a rather good correlation to that of the sub-ablation emission yield for GaAs(110), suggesting that the reduction of the ALF can be ascribed to the onset of the transition involving surface intrinsic states. We have presented a mechanism to interpret the photon-energy dependences for the laser-induced defect-initiated atomic emission from the GaP(110) and GaAs(110) surfaces on the basis of the band structures of bulk and surface and the interaction of defect states with the bulk and surface intrinsic states.

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