Defect-excitation processes involved in laser-induced atomic emission and laser ablation of nonmetallic solids

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A microscopic theory of defect-induced emission of atoms from nonmetallic surfaces is presented. The results agree very well with the experimental results for the emission yield with the number of laser shots, laser fluence, and incident photon energy. Our results show that the emission of atoms at low photon energy and laser fluence originates only from the surface defects like adatoms and steps. Such emissions cannot be observed from the defect-free surfaces of semiconductors considered here.

I. INTRODUCTION

Laser ablation of nonmetallic solids has become an active field of research[1-5] because of its wide industrial applications. When laser pulses of adequate fluence are incident at crystalline surfaces, a massive emission of atoms is induced, resulting in surface damage. The process is usually called laser ablation or laser sputtering, and it has been observed in metals,[6] nonmetallic inorganic solids including semiconductors,[4] and insulators[5] and organic solids such as polymers.[7]

Two causes have been put forward for the process of laser ablation: (1) surface bonds are broken due to the high density of electronic excitations caused by the absorption of laser photons,[8] and (2) atoms are emitted due to thermal melting of the surface caused by the intense laser beams.[9] The mechanism (1) is supported by the theory[10-13] that under a high density of excitations a strong charge-carrier–phonon interaction can cause a pairing of holes on the same bond, because such a paired hole state is energetically more favorable. The localization of a pair of holes on a covalent bond means the removal of its bonding electrons, and therefore such a bond is broken. It has been suggested that the ablation is initiated by the emission of weakly bonded atoms (WBAs) from vacancies, which results in the evolution of vacancy clusters on the surface, enhancing the emission further and leading finally to ablation.[14] The thermal mechanism (2) is suggested on the assumption that the energy of electronic excitation induced by surface-laser photon interaction is converted into thermal energy instantaneously.

Recent measurements, with a detection sensitivity of 10^{-6} monolayer, has revealed that the constituent atoms of Si,[15] GaP,[16-19] and GaAs (Refs. 20 and 21) are emitted by the nanosecond laser-pulse irradiation even below the ablation threshold. Three different experimental observations have been made to study the dependence of the emission yield Y on the (i) number of laser pulses, n, incident on the same location of the surface, shown in Fig. 1; (ii) the laser fluence F, shown in Fig. 2; and (iii) the photon energy, shown in Fig. 3. Based on these results, it has been shown that the emission, detected by submonolayer sensitivity, is due to the bond breaking of WBAs as defects on surfaces.

As shown in Fig. 1, at a fluence of 1 J/cm^2 for the GaP(110) surface, Y first decreases rather rapidly with n up to 50–70, and then the decrease is slowed down for $50 < n < 200$. After increasing the laser fluence from 1 to 1.3 J/cm^2, Y increases with n. Repeated irradiation at this laser fluence modifies the surface structure as detected by the low-energy electron diffraction (LEED), i.e., the LEED pattern observed before the irradiation disappears after the irradiation. On the other hand, no change in the LEED pattern is observed by repeated irradiation for the fluence range where Y decreases with n. Such a change in Y-n relation with increasing F is very distinct and observed in all materials studied. Therefore the fluence between the decreasing and increasing Y-n relations is defined as the threshold ablation laser fluence and

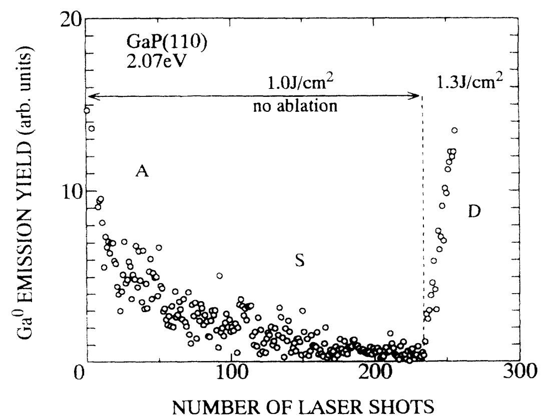

FIG. 1. The yield Y of emission of Ga^0 induced by repeated irradiation of the GaP (110) surface with 2.07-eV laser pulse of 20-ns duration, and of fluences 1.0 and 1.3 J/cm^2, as a function of the number of shots, n, incident on the same spot (Ref. 21).

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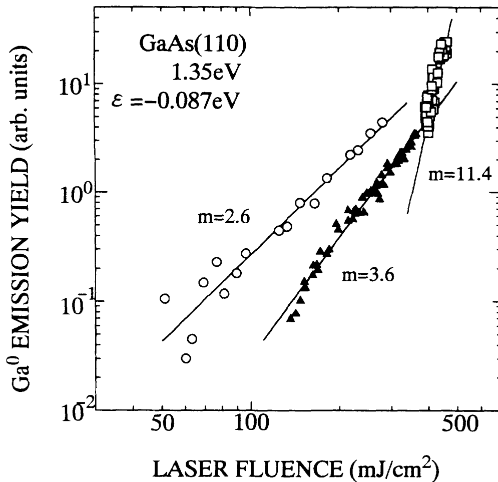

FIG. 2. The yield Y of emission of Ga^0 atoms induced by laser irradiation of the GaAs(110) surface with 1.35-eV laser pulses of 20-ns duration, as a function of the laser fluence F (Ref. 21).

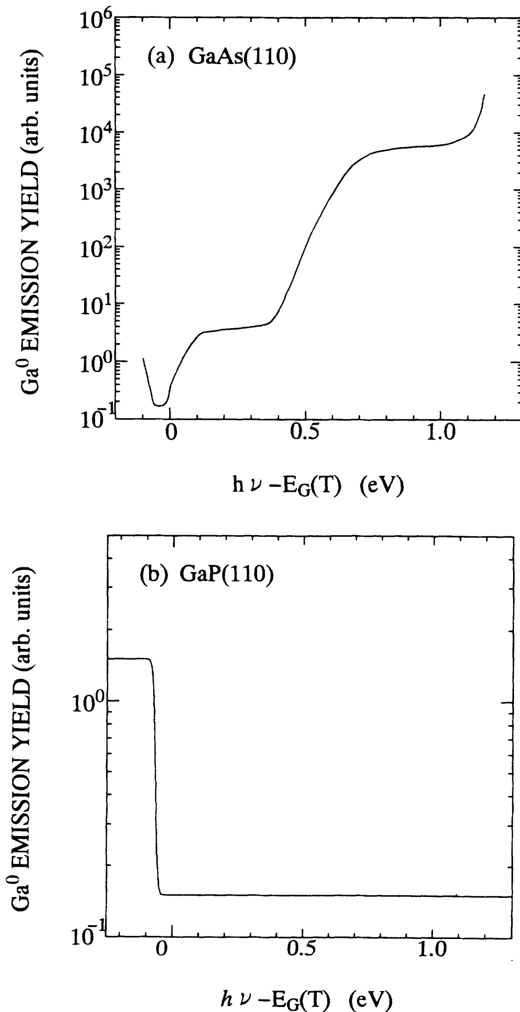

FIG. 3. Schematic illustration of the photon energy dependence of the yield Y of Ga^0 atoms emitted by 20-ns laser irradiation of (a) the GaAs(110) surface and (b) the GaP(110) surface (Ref. 21).

denoted by F_{th}. It has been shown recently[22] that F_{th} thus determined is closely correlated with the threshold ablation laser fluence required for the macroscopic[2] damage of a surface. Hattori *et al.*[16] assigned the emission giving rise to a rapidly decreasing Y-n relation as the A component and that to a slowly decreasing Y-n relation as the S component. They suggested that the A and S components originate from excitations of adatoms and WBAs on step-type defects, respectively, because one obtains a perfect surface after the emission of an adatom, while emission of a WBA from a step may produce the same type of defect as that before the emission. The experimental values of n in the A and S regions, as mentioned above, has been attributed to the number of excitations required to break the bond of WBAs. As a matter of convention, the emission of atoms below F_{th} (A and S components) is called subablation, and that above F_{th} ablation.

The Y-F relation, shown in Fig. 2, represents a typical superlinear dependence of Y on F in both subablation and ablation regions.[17] The Y-F relation in the subablation region can be expressed as $Y \propto F^m$, $m = 2-4$ for the A component, and 4–7 for the S component. A larger power index, $m = 10-15$, has been observed above the ablation threshold. The large value of m above the ablation threshold has been attributed to the evolution of the vacancy clusters,[14] and it has been pointed out that the value of the power index above the ablation threshold is close to that for the S component, if the change in the number of WBAs by formation of the vacancy clusters is properly accounted for.

Figure 3, which represents the photon energy dependence for the S component, shows that Y decreases rapidly at photon energies approaching the band-gap energy in both GaAs and GaP, and then it rises in steps in GaAs, but remains nearly constant in GaP. The cause of the emission at photon energies below the bulk band-gap energy and its subsequent decrease at photon energies near the band-gap energy has been addressed by both Kanasaki *et al.*[19] and Okano *et al.*,[21] but it is not yet fully understood. Nevertheless, it is nearly impossible to believe that the emission observed below the band-gap energy is due to heating, because the optical-absorption coefficient is extremely small and therefore most of the incident photons are transmitted through the specimen. Moreover, the effect of heating can explain neither the decrease in the emission yield near the band-gap energy nor the difference in the emission yield of Ga^0 observed from the GaP(100) and GaAs(100) surfaces above the band-gap energy; that is, in GaAs the yield increases in steps, whereas in GaP it remains constant.

In this paper, a microscopic approach is followed based on the experimental results shown in Figs. 1–3. The present approach provides a microscopic mechanism for the emission of Ga^0 originating from breaking of the bonds of WBAs and a semiquantitative analysis of the dependence of Y on photon energies. It is asserted conclusively that the origin of the subablation emission and ablation in its primary stage is due completely to excitation of defect electronic states.

Although the approach presented here can be applied

to both the subablation emission and ablation of nonmetallic solids in general, in this paper we will focus only on materials such as semiconductors and alumina, in which the defects on the surface are considered to be responsible for the emission. We will discuss below the difference between the mechanism of laser-induced emission in these materials and that of the other group of materials, in which the emission is not necessarily related to defects. Most complete studies of the dependence of Y on photon energy have been carried out in GaP and GaAs. However, the behavior of laser-induced emission of Si, as far as Y-n and Y-F relations are concerned, is similar to that of GaP and GaAs.[15] Also, the crystal structures of these materials are similar, therefore here we will use Si for microscopic analysis of the problems common to these three materials.

II. MICROSCOPIC CONSIDERATION OF DEFECT STATES

It is important for any mechanism of laser-induced subablation emission to be able to explain both the breaking of bonds and emission of neutral atoms. For this reason it is also very important to understand the electronic structure and bonding of defects like adatoms, steps, and vacancies on a surface, which will be described briefly below.

A. Electronic energy states of surface adatoms

On the basis of the theory developed[23] for semiconductor surfaces, it is expected that the semiconductors considered here have their surface occupied states, consisting of bonding orbitals of surface dangling bonds, near but below the valence-band edge and the unoccupied states above the conduction-band edge. These surface states of bonding, S_b, and antibonding, S_a, are schematically illustrated in Fig. 4. Also, the bonding D_b and antibonding D_a states of an adatom at the surface are considered to be localized within the band gap, near the edges of the valence and conduction bands, respectively, as shown in Fig. 4. We have also shown in Fig. 4 the singly occupied dangling-bond states of the surface and those of an adatom, denoted by D_h, located near the middle of the band gap.

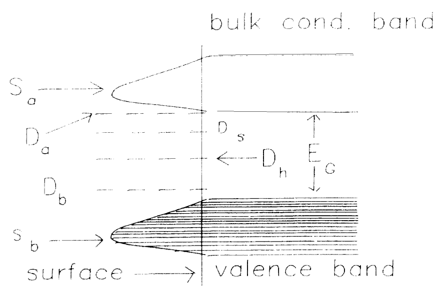

FIG. 4. Schematic illustration of the surface states (S_b: occupied, S_a: unoccupied), defect bonding (D_b), defect antibonding (D_a), and singly occupied dangling bond (D_h) states for (110) surfaces of Si, GaP, and GaAs crystals.

B. Electronic energy states of defects like steps and vacancies on a surface

In addition to adatoms, a surface usually has defects like steps and vacancies. The atoms at the edges of a step and vacancy will also have additional dangling-bond states. These dangling-bond states of both steps and vacancies will also be localized at the surface, and the energy of such states will be within the bulk band gap. As each step and vacancy can have several partially coordinated atoms interacting with each other, we expect that their dangling-bond states will lie within the top half of the band gap due to reconstruction. These states, denoted as D_s, are also shown in Fig. 4.

C. Bond breaking under intense laser irradiation

The breaking of a covalent bond can occur due to localization of a pair of holes on a bond under intense laser irradiation due to strong electron-lattice interaction. We have shown that the state with a localized pair of holes is more favorable energetically.[10-12] Here we will use this result to address the mechanism of the localization of two holes under a high density of excitations induced by laser irradiation.

The lowering of the energy of excitation due to the pairing of two holes on a bond under strong carrier-phonon interaction is given by[11]

$$\Delta E = 2E_p + E_{hp} \ , \tag{1}$$

where E_p is the lattice relaxation energy due to the localization of an electron, and E_{hp} is that due to localization of a pair of holes on a bond, given by

$$E_{hp} = \frac{\sum_j \left[\frac{1}{M} (A^{jh}/\omega_j)^2 \right]^2}{3 \sum_{j'} T_{j'}} \ , \tag{2}$$

where M is the ionic mass, A^{jh} the force constant, and ω_j the frequency of vibration of the jth phonon mode ($j = x$, y, and z). $T_{j'}$ ($j' = x$ and y) is the nearest-neighbor transfer integrals in the x and y directions. (In this calculation it is assumed that the surface is in the xy plane.[11]) Depending on the strength of the lattice interaction A^{jh} and other parameters, the lowering of energy can be up to the order of a few eV.

In this view, therefore, if one can localize a pair of holes in the bonding state of an adatom, the bond will be broken and the adatom will become free. The excess energy equal to ΔE in (1) may provide the thus freed atom with the kinetic energy to move it away from the surface. It is expected here that the condition of strong carrier-phonon interaction can easily be met at a site of WBA, because an adatom-type defect is only loosely bound onto the surface. This will favor the pairing of holes as discussed above,[11,12] and consequently the bonds of such WBA's will be broken first. This is also in accordance with the effect of $-U$ potential suggested by Anderson,[24] which has been applied to explain the relaxation of the semiconductor vacancy in the bulk.[25,26]

There are several possible ways of producing two holes localized on a defect bonding orbital: e.g., (i) successive excitation of both the bonding electrons either to the nonbonding orbitals of the same defect, or to the surface unoccupied states or to the bulk conduction band; (ii) subsequent localization of two holes on a defect bonding orbital, after being transferred from the surface occupied states where they were created first by laser irradiation; or (iii) any combinations of (i) and (ii). In any case, after localizing a hole on the defect bonding orbital, one expects the formation of a metastable state, in which the corresponding covalent bond is enlarged, giving rise to a localized singly occupied state within the energy gap. Such a metastable state of a localized hole can be formed within a time equal to the inverse of the characteristic lattice frequency, and therefore the localization of the second hole can take place within the duration of a single laser pulse.

It should be noted, however, that the condition of paired-hole localization on a defect bonding orbital, although necessary for breaking a bond, does not guarantee the neutrality of thus emitted atoms from the surface as observed experimentally. Using the example of a silicon surface, this will be addressed in what follows.

D. Conditions for emission of neutral atoms

When the covalent bond of a Si adatom is broken due to the localization of a pair of holes, the outgoing adatom thus freed can be positively charged. In Fig. 5 are shown the silicon bulk energy bands, and surface and adatom localized energy states, along with the electrostatic potential due to a Si^+ ion at the surface. In drawing Fig. 5, the following values are taken into account: Si work function $W = 5$ eV, and a length of bond of the adatom of 2.3 Å. Thus the interaction potential should intersect the bulk states at an energy $E_s = 3.1$ eV below the bulk continuum (Fig. 5).

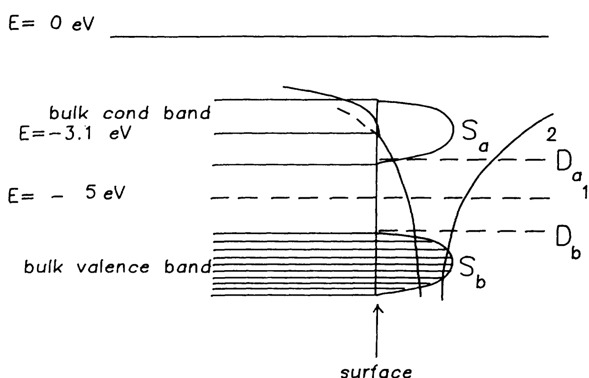

FIG. 5. Schematic illustration of the Coulomb interaction between a freed atom (Ga^+) at the surface and surface electrons. Location 1 represents the level of the work function for Si at $E = -5$ eV, 2 represents the Coulomb potential, and D_a and D_b denote the antibonding and bonding states of a weakly bonded atom at the surface, respectively. S_a and S_b represent the surface unoccupied and occupied states, respectively. The level at $E = -3.1$ eV represents the location of the point of intersection of the Coulomb potential with the conduction band on the energy scale.

When both bonding electrons of the adatom are excited to the unoccupied surface states, namely from D_b to D_a or S_a (Fig. 5), the outgoing Si^+ will have a stronger interaction with the electrons in the S_a or D_a states, which extend spatially outside the surface and hence are closer to the surface, than the electrons in the bulk conduction band. Thus as the Si^+ moves away from the surface, the electron in S_a states is transferred to D_a states, eventually resulting in emission of a neutral Si atom.

Another interesting point arises here: if the bonding electrons are excited to the bulk conduction band, they will relax quickly to the bottom edge of the conduction band; then the outgoing atom cannot capture the electron from the conduction band, because the electron will have to tunnel through a potential barrier between the surface and the outgoing atom. The height of the potential barrier is about 0.7 eV, and its width is 0.4 Å. This gives a rate of tunneling of 10^8 s^{-1}, which is too slow to be effective in a process as fast as laser ablation.

III. PHOTON ENERGY DEPENDENCE OF THE EMISSION YIELD

Here it is appropriate first to define an energy parameter E as $E = h\nu - E_G(T)$, used in the experiments, where $h\nu$ is the incident photon energy and $E_G(T)$ is the bulk band-gap energy at a temperature T K. This gives three regions for E: $E < 0$, $E \approx 0$, and $E > 0$, corresponding to the photon energy being below, near, and above the band-gap energy, respectively. We will address the three cases one by one below.

A. Photon energy below the band-gap energy, $E < 0$

From Fig. 4 it is obvious that the only electronic transitions on the surface that can be induced by such photon energies are from the defect bonding orbitals (D_b) to the defect dangling-bond states (D_h), antibonding defect orbitals (D_a), surface unoccupied states (S_a), and the bulk conduction band. Assuming that the duration of a laser pulse is t, the number of times a single atom on the surface can be hit by photons, one after the other, can be given by $\sigma\phi t$, where σ is the cross section for a single excitation, and ϕ is the photon flux. In the experimental setup being considered here, the duration of an incident laser pulse is ≈ 10 ns, $\sigma \approx 10^{-17}$ cm^2, and the laser fluence $\sigma t \approx 10^{18}$ cm^{-2}. Therefore an atom is expected to be excited by photons several times within the duration of a laser pulse.

Consider the specific case of an adatom of Si with three dangling bonds and one covalent bond on the surface, as shown in Fig. 6. Supposing the first photon hits the adatom and excites its bonding electron from the bonding to antibonding states near the conduction-band edge, as shown in Fig. 6(a). Before the adatom is hit again by another photon, a relaxation is expected to occur in the energy states involved due to strong carrier-phonon interaction. This is illustrated in Fig. 6(b) by moving the singly occupied bonding state thus created above the top

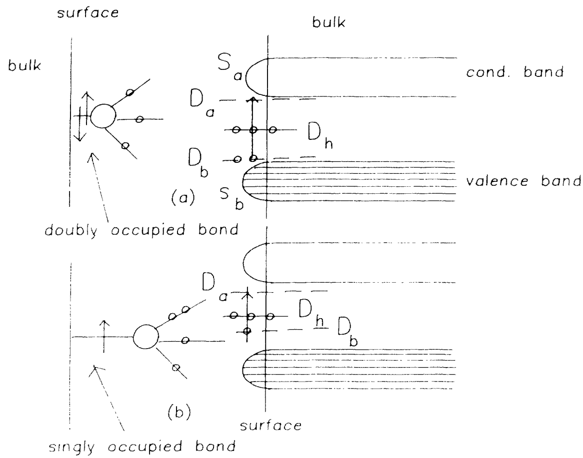

FIG. 6. Schematic illustration of the excitation of an electron from the bonding state (D_b) of a weakly bonded atom at the surface to the antibonding state (D_a) or the unoccupied surface states (S_a), and subsequent relaxation of the bonding and antibonding states. (a) represents a doubly occupied bonding orbital near the valence-band edge of the bulk, and three dangling bonds and their energy states (D_h). (b) represents the excitation of one of the electrons from the bonding orbital to the antibonding orbital or surface unoccupied states, resulting into pushing the singly occupied bonding orbital thus created above the valence-band edge and the antibonding orbital below the conduction-band edge. It is expected that when both the electrons are exited into the dangling-bond–antibonding electron states, the separation between the antibonding and bonding orbital vanishes and both states merge into the hybrid dangling-bond states because the bond is broken.

of the valence band, because such relaxation is expected to occur within the picosecond time scale. When the second bonding electron is excited by another photon, the covalent bond will be broken due to localization of the two holes on the same bond. As stated in Sec. III, process (i) may play the dominant role in moving a neutral atom away from the surface.

In a similar way, the emission of other defect atoms, such as doubly bonded adatoms on steps, can be explained. However, in such cases absorption of more than the minimum number of two photons will be essential for breaking all their bonds. This point will be elaborated further below.

B. Photon energy near and above the band-gap energy, $E \geq 0$

As the photon energy increases and approaches the band-gap energy, it becomes resonant with the bulk excitation energy. In this case the following two processes can take place: (1) Excitations created on the surface will resonantly transfer their energy to the bulk excitation states; and (2) along with surface excitations, bulk excitations also will be created. Process (2) cannot be considered to be effective in the emission.[16] The consequence of process (1) would be that the excitations thus created will be transferred into the bulk without contributing to any emission yield. Therefore the emission yield will be reduced at photon energies near the band-gap energy.

The rate of transfer of energy, R, from the defect to the bulk excited states can be written as

$$R \propto |\langle \Psi_I|\mathbf{H}_I|\Psi_F\rangle|^2 \rho_F(E_F) \ , \tag{3}$$

where $\langle \Psi_I|\mathbf{H}_I|\Psi_F\rangle$ is the resonance transfer transition matrix element, and $\mathbf{H}_I$ is the total electron-electron interaction energy operator between the outer orbital electrons of the defect atom and valance-band bulk electrons. $\Psi_I = \psi'_d\psi_b$ is the wave function of the initial state, as a product of the wave function of an excited defect-localized state, ψ'_d, and that of the bulk ground state, ψ_b; and $\Psi_F = \psi_d\psi'_b$ is that of the final state as a product of the wave function of the ground defect state, ψ_d, and bulk excited state, ψ'_b. Here the primed wave functions denote the excited states. It also should be noted that the bulk wave function is the antisymmetrized product of the Bloch functions. For the calculation of the transition matrix element, however, one has to write the Bloch functions as a Fourier transform of the localized Wannier functions. $\rho(E_F)$ is the density of the final states.

Dexter[27] has shown that the transition matrix element $\langle \Psi_I|\mathbf{H}_I|\Psi_F\rangle$ is proportional to the oscillator strength of individual transitions, normalized absorption curve areas, and the overlap between the absorption curves corresponding to the optical dipole moment transition from the ground to the defect-localized excited state (ψ'_d) and that from the ground to the defect-perturbed bulk excited state (ψ'_b); each curve should be normalized with respect to its total area. The oscillator strength for the optical transition from an isoelectronic impurity state to the continuum should show a broad spectrum starting from E_1, the energy difference between the defect energy level and the bottom of the continuum, as shown in Fig. 7. It is well known that the photon energy dependence of the optical absorption in the bulk exciton states in a direct semiconductor has a resonance peak, as shown in Fig. 7(a). Faulkner[28] calculated the optical-absorption curve to produce excitons localized by the isoelectronic impurities in GaP crystals, and obtained a broad spectrum starting from the indirect exciton energy to higher energies. As the adatoms are similar to isoelectronic impurities, it is assumed that the photon energy dependence of the transition dipoles for the formation of the localized exciton is valid for adatoms as well. In Fig. 7 we show schematically the optical-absorption curves relevant to the resonance energy transfer for both direct [Fig. 7(a)] and indirect [Fig. 7(b)] semiconductors.

It is important to note that the principle of conservation of momenta only allows the energy transfer from the localized surface defect-excited states to the localized bulk exciton states. In direct semiconductors, most of the absorption in the localized bulk exciton states takes place at the band edge, as is obvious from the resonance absorption peak shown in Fig. 7(a). It should be reemphasized here that the area under each of the absorption curves in Fig. 7 has to be normalized to unity. Therefore, according to Dexter's theory, the resonance transfer from the defect-excited state to the bulk exciton states is only limited to the band edge. Consequently, one expects that the excitation of the defect-excited states by photons of

energy $E > 0$ will lead to the emission, because the rate of the transfer of energy from defect to bulk-localized states is very small in this energy range in direct semiconductors. This explains quite well the observed increase in the emission yield in GaAs for photon energy $E > 0$, as shown in Fig. 3(a).

On the other hand, as stated above, for indirect semiconductors the optical absorption in the bulk-localized exciton states starts near the band-gap energy and extends to $E > 0$. That means, even though the surface defect states are excited by photons with energy $E > 0$, this energy is transferred to the bulk-localized exciton states, because according to Dexter's theory, the rate of such energy transfer is expected to be very high in indirect semiconductors. Therefore, no increase in the emission yield can be expected for photon energy $E > 0$ in indirect semiconductors, as indeed observed in GaP [Fig. 3(b)].

It is well established that the surface electronic states

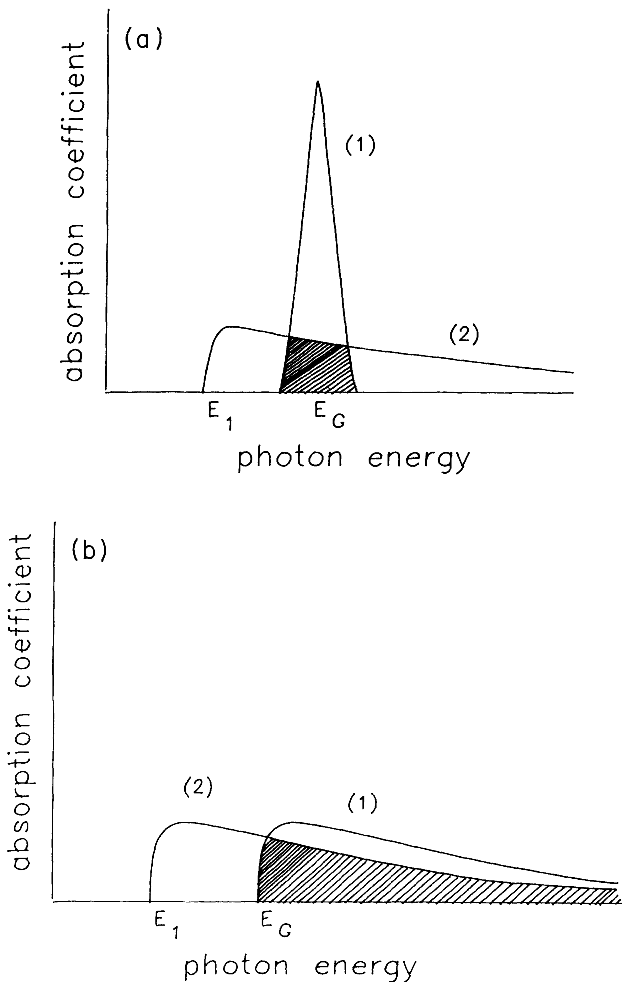

FIG. 7. Schematic illustration of the difference between the absorption coefficient curves for the localized bulk exciton states (1) and surface defect states (2) in (a) direct-band-gap semiconductor like GaAs and (b) indirect-band-gap semiconductor like Si and GaP. The shaded areas denote the overlapping areas to which the rate of energy transfer is assumed to be proportional.

in most semiconductors lie close to the bulk energy bands as shown in Fig. 4, though there is some controversy over the case of GaP. However, recent experimental results of Chiaradia *et al.*[29] have shown that GaP also has surface states close to the bulk energy bands. Keeping this in mind, it is expected that the increase in the emission yield in GaAs, at photon energies above the band gap, corresponds to the optical transition energy from S_b to S_a and to the bulk continuum, indicating that the increase is due to creation of holes in the surface defect-localized states. The dynamics of such excited holes in the surface is essentially two dimensional in character, so the holes remain localized in the surface states until colliding with phonons to acquire momentum perpendicular to the surface into the bulk. Since the cross section for the interaction of a particle confined in a two-dimensional surface with a defect is high, such confinement in conjunction with strong carrier-phonon interaction will be able to enhance the probability of localization of two holes on the bonding orbitals. Therefore, also as a result of the confinement, the emission yield should increase for photon energies above the band-gap energy for direct semiconductors. However, for GaP the resonance energy transfer to the bulk is considered to dominate such enhancement in yield due to confinement.

IV. DISCUSSION

We have presented a microscopic approach to study the processes of laser-induced ablation from semiconductor surfaces. In particular, the emission of Ga^0 atoms observed[15–20] from the (110) surface of GaAs and GaP is considered. The results presented here agree with experimental results and predictions, and, in addition, develop a microscopic understanding of the mechanism of emission of neutral atoms induced by laser irradiation on semiconductor surfaces, particularly at low photon energy and laser fluence.

On the basis of microscopic considerations presented here (Figs. 5 and 6), it is found that the emission of a WBA as an adatom from a surface, induced by laser photons of energy less than the band-gap energy, occurs due to excitations of the defect bonding state electrons to the unoccupied localized surface defect states near the edge of the conduction band or into the continuum. Under the influence of high excitation density and strong carrier-phonon interaction, the pairing of holes on the same bond is energetically more favorable.[10–12] This more favorably allows the excitation of both bonded electrons on a covalent bond by laser pulses. From a laser pulse the incident photons are absorbed in cascade-type excitations, one after the other. That means both covalent electrons are not excited simultaneously, but one after the other. After the first excitation of a relaxation in the energy of excitation will occur due to electron-lattice interaction, before the second bonding electron is excited by another incident photon. A relaxation in the excitation energy will take place again, helping the freed atom moving away from the surface. On its way out of the surface the atom will recapture an electron and its neutrality will be retained, as explained in Sec. III (Fig.

5). However, it should be noted that the paired-hole state on a bond is not a stable state and therefore cannot be observed in any form other than the emission yield resulting from such bond breaking.

From the above discussion it should very clearly be understood that at photon energies below the band-gap energy and low laser fluence (subablation region) the emission of Ga^0 atoms can only originate from surface defects like adatoms. At such low photon energies the thermal effect cannot play any role in the emission. Also, the perfect surface atoms cannot be emitted at such low laser fluence and photon energy. The process is therefore completely defect oriented.

In view of the above arguments, it is clear that at least two excitations during a pulse are needed for breaking the bonds of an adatom, leading to a quadratic *Y-F* relation.[17] Accordingly, the *Y-F* relation for doubly bonded WBA's on steps would be $Y \propto F^4$, and for triply bonded WBA's around vacancies it would be $Y \propto F^6$. It has been found experimentally that the value of m for WBA's as adatoms is 2–4, that for WBA's on steps is 4–6, and that for WBA's around vacancies is 10–15. Thus the lowest $m=2$ for adatoms and $m=4$ for steps agree with our expectations from theory quite well. The higher values of m may appear due to transitions, which cannot create a hole on the bonding defect orbital directly.

For the case of a vacancy, one can write the emission yield Y as[13]

$$Y = N_d(F)\left[\prod_{i=1}^{6}\sigma_i\right]F^6 , \tag{4}$$

where $N_d(F)$ is expected to increase with F due to the evolution of a vacancy cluster as[18]

$$N_d(F) = N_0 F^6 , \tag{5}$$

where N_0 can be regarded as the initial number of WBA's around vacancies. Thus from (4) and (5), we obtain

$$Y \propto N_0\left[\prod_{i=1}^{6}\sigma_i\right]F^{12} . \tag{6}$$

This agrees reasonably well with the experimental result, $Y \propto F^{10-15}$, for ablation originating from vacancies. Although the surface atoms on the perfect sites are also triply bonded as the WBA's around vacancies, their excitation can create only delocalized charge carriers in the bulk states, and the localization of a paired hole on a bond will not be possible. Therefore, no emission can be expected to occur in this situation.

The process of emission of atoms as presented in this paper is induced by localization of two holes on the defect bonding orbitals at the surface. Accordingly, if a surface does not have any defect, no emission should be observed. Thus the defect-oriented mechanism of emission as presented here is very different from that applicable to those solids where very strong electron-lattice coupling exists, causing self-trapping of excitons even on a perfect surface. A well-known example of this type of solid is that of alkali halides, in which the emission is linearly proportional to the laser fluence and can be observed even at very low fluence.[30,31]

It may be desirable to mention here that the electronic structure of defects on surfaces and lattice relaxation after their excitation is an interesting area for experimental investigation; the excitation spectroscopy for laser-induced emission and *in situ* observation of the STM images can provide direct information about the relaxation. Theoretically, the study of defect electronic states on the surface is a new area of research interest; the coupling strength between the bulk and surface electronic states can vary depending on the type of defect and its interaction with both the two-dimensional surface continuum and three-dimensional bulk continuum states. The experimental observation of defect electronic states with photons of energy above the band-gap energy is scanty, because the photons cannot reach defects located within the bulk. The defects on the surface can be surveyed with photons of any energy, and therefore further experimental work on the interaction of defect states with two- and three-dimensional continuum states will be of interest.

V. CONCLUSION

From the microscopic approach followed here, it is clear that the origin of emission at low laser fluence is primarily due to excitation and paired localization of holes in the defect bonding states. Such emission cannot occur from a defect-free surface. The observed dependence of the emission yield on the incident photon energy in both subablation and ablation regions has been successfully explained.

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