

Structural Change Induced by Electronic Excitation on GaP Surfaces

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Structural change of GaP($\bar{1}\bar{1}\bar{1}$) surfaces induced by irradiation with laser pulses in the photon energy region between the indirect and direct band gaps has been investigated. A dip was found near the indirect band-gap energy in the relation between the photon energy and the threshold laser fluence above which the change from the (17×17) reconstructed structure to the (1×1) structure occurs. It is concluded that the structural change induced by laser pulses near the indirect band-gap photon energy is due to surface electronic excitation.

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Desorption and associated surface modification induced by electronic transition is a topic of current interest. It is well established that core excitation of several metal-adsorbate systems leads to desorption. It has been shown recently that valence electron excitation of some metal-adsorbate systems leads to desorption, of which the mechanism is less clear. For the surface of bulk materials, desorption induced by valence-electron excitation is known only for limited insulators, such as alkali halides.¹ It is not yet clear whether excitation of valence electrons of other insulators and semiconductors causes desorption.

For desorption and surface modification to be induced by electronic excitation, energy imparted to the electronic system should be transferred to atomic energy that results in desorption. Such energy conversion, originating from strong electron-phonon interaction, is known to cause local structural changes in the bulk of certain nonmetallic solids.^{2,3} The most well documented example is defect formation from excitons in alkali halides,⁴ in which self-trapping of an exciton and subsequent isomeric transformation, arising from the adiabatic instability at the self-trapped configuration, results in Frenkel pairs comprising a halogen vacancy (an F center) and an interstitial halogen atom (an H center). The same instability is considered to cause desorption in alkali halides.

It is of interest to seek whether desorption and associated surface modification take place by excitation of valence electrons on the surfaces of the substances in which no bulk photoinduced structural change occurs.¹ Such studies may reveal the nature of electron-lattice coupling, specific to the surfaces, which leads to desorption and the surface modification. There is fragmental information on desorption induced by electronic excitation of nonthermal origin in materials, in which no defects are formed in the bulk by electronic excitation. For example, studies of excimer-laser-induced desorption from Al_2O_3 by means of laser-induced fluorescence⁵ show that the vibrational energy of AlO molecules desorbed is independent of laser intensity and is much lower than that of Al_2O_3 at the melting point. The photon energy dependence of laser-induced desorption from

GaP has been shown to exhibit a prominent peak at the indirect band-gap energy,⁶ and the peak is ascribed to the desorption induced by photon absorption at the damaged surface layers. Less convincingly, laser-induced modifications of surface layers determined by means of electron microscopy,⁷ optical reflection and absorption measurements,⁸ and Rutherford backscattering⁹ have been ascribed also to the effects of electronic excitation.

The experiments described above were all carried out on uncharacterized surfaces. For desorption experiments, it is often the case that the surface is damaged substantially during measurements. Recently we have reported LEED observations of the structural change induced by irradiation with nanosecond laser pulses near the indirect band-gap energy.¹⁰ The results show that structural change is induced in clean surfaces under an experimental condition where the temperature rise is not significant. The type of electronic excitation giving rise to the structural change, however, is not yet clear. The most direct way to make clear the nature of the electronic excitation leading to structural change is to measure its wavelength dependence. An indirect band-gap semiconductor like GaP is particularly convenient for this type of study, since the optical absorption coefficient at the indirect band gap for the bulk is small, but that at the surface is high because of the violation of the wave number selection rule.

We present here the experimental results of the wavelength dependence in the threshold laser fluence above which the conversion from the clean (17×17) reconstructed surface to the (1×1) structure takes place. We found that the threshold laser fluence has a dip near the indirect band gap, indicating that photons near the indirect band gap, at which the bulk optical absorption coefficient is extremely small, are particularly effective in causing a structural change. The results present clear evidence that modification of clean surface occurs by surface electronic excitation.

Clean GaP($\bar{1}\bar{1}\bar{1}$) surfaces were prepared from an n -type S-doped crystal as described already¹⁰ and shown to exhibit a (17×17) reconstructed structure¹¹ by LEED measurements. Laser pulses of 20-ns duration, generated with an excimer-laser-pumped dye laser, were in-

cident on specimens. The intensity of the laser pulses was monitored during irradiation with a photodiode calibrated by means of a calorimeter. LEED measurements were performed after irradiation with a single laser pulse or with multiple laser pulses of a fixed fluence. The size of the laser beam on the specimens was 1.4 mm in diameter and for LEED measurements an electron beam of a size of 0.6 mm in diameter was incident within the laser-irradiated region. In order to achieve measurements for several laser fluences on a surface, the specimen was shifted so that a new surface region is subjected to subsequent irradiation.

Figure 1 shows the relation between the laser fluence and changes in the LEED patterns after irradiation with a single, a hundred, and a thousand laser pulses of wavelengths of 440, 480, and 540 nm. The repetition rate is 10 Hz. The area indicated by (17×17) shows the range

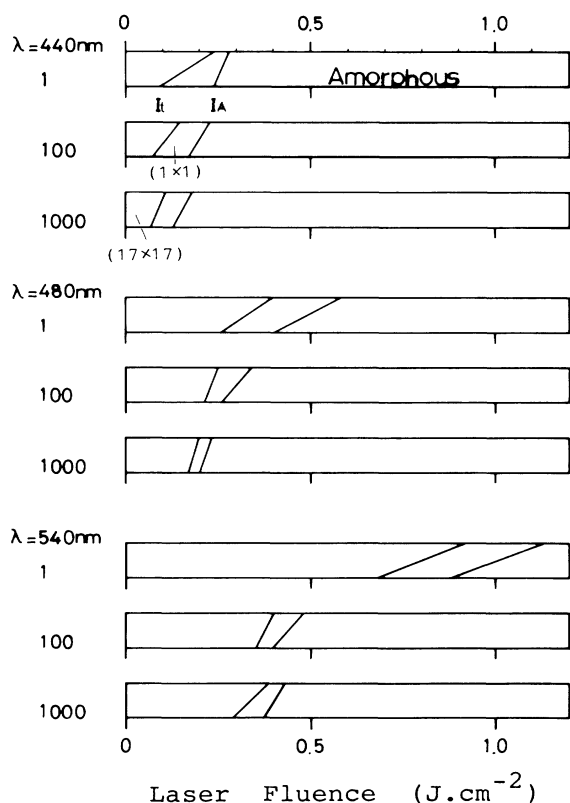


FIG. 1. Structures of GaP(111) surfaces after irradiation with a single, a hundred, and a thousand laser pulses of several wavelengths. The abscissa indicates the laser fluence. In each column, the area at the left [denoted by (17×17) in the top figure] is the region where no transformation was observed, that at the middle [denoted by (1×1) in the top figure] is the region where transformation to the (1×1) structure was observed, and that at the right [denoted by amorphous in the top figure] is the region where no crystalline order was observed. The nonvertical lines at the boundary indicate the experimental ambiguity of the threshold laser fluence.

of fluence where no change in the surface structure took place, while that by (1×1) shows the range of fluence where transformation to the (1×1) structure occurred. Further increase in the laser fluence produced conversion to amorphous surfaces as indicated by amorphous in the figure.

The transformations from the (17×17) structure to the (1×1) structure and that from the (1×1) structure to the amorphous are gradual: The intensities of the spots representing each structure decrease gradually as the laser fluence increases. Nonvertical boundaries in Fig. 1 indicate the range where the weakest LEED spots representing (17×17) and (1×1) structures disappeared, while the most intense LEED spots remained. The fluence at which the weakest LEED spot representing the (17×17) and (1×1) structure disappears is called threshold fluence hereafter. It is clear from the results that an increase in the repetition of laser pulses reduces the laser fluences where the transformations to the (1×1) structure and amorphous take place. The reduction is more dominant for irradiation with indirect band-gap photons (540 nm) than that with direct band-gap photons (440 nm).

The wavelength dependence of the laser fluence that causes transformation to the (1×1) structure after irradiation with a hundred pulses is shown in Fig. 2. It is

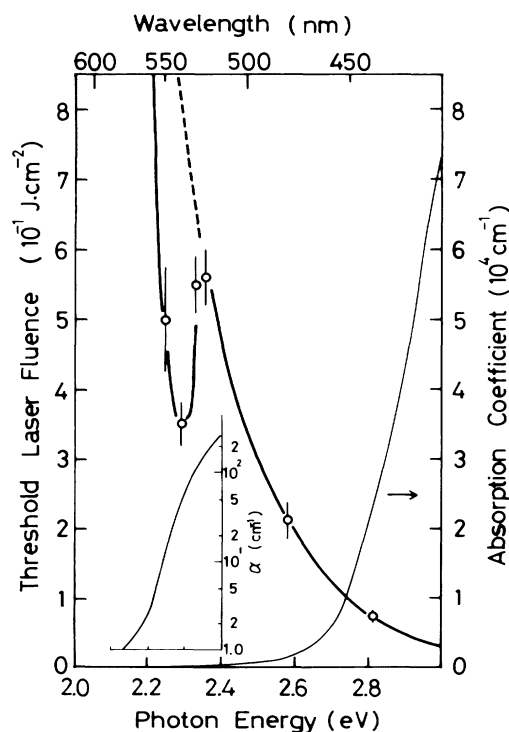


FIG. 2. Dependence of the threshold laser fluence to the (1×1) structure on the photon energy, obtained after repetition of laser pulses a hundred times. The thin solid curves show the bulk optical-absorption coefficient of GaP.

clear that a dip is observed at the indirect band-gap energy in the relation between the threshold fluence and the photon energy, besides a gradual decrease in the threshold laser fluence as the photon energy increases from the indirect band gap to the direct band gap.

Using the experimental results described above, first we show that the difference in the threshold laser fluence at the direct band-gap and the indirect band-gap photon energies cannot be explained in terms of the thermal process. Since the bulk absorption coefficients at the direct and indirect photon energies differ by a factor of 200, the temperature rise at the surface layers induced by a laser pulse of the same fluence is smaller for the indirect band-gap photons at least by the same factor. The melt threshold of GaP for a 15-ns laser pulse of direct band-gap photons has been shown to be about 0.3 J/cm^2 . Thus no bulk temperature rise should occur by irradiation with a 20-ns laser pulse of indirect band-gap photons at the same fluence. It would be the case that the first few layers of the surface have a high optical absorption coefficient for the indirect band-gap photons, because of violation of the wave-number selection rule, as demonstrated by theoretical calculations for surface electronic structures¹² for the (110) surfaces of GaP. Using the thermal diffusivity of GaP at room temperature, $0.1 \text{ cm}^2 \text{ s}^{-1}$, however, we obtained the thermal diffusion length during the laser pulse of 4000 \AA . Thus the energy absorbed at the surface layer will immediately be diffused and hence will not contribute to any temperature rise. In fact, a temperature rise of 5° was obtained by a calculation under an assumption that only the surface layer absorbs photons at a cross section the same as that of a bulk layer for direct band-gap photons. If the structural change is induced by a thermal effect, namely by vaporization, the difference in the threshold fluences for the indirect and direct band-gap photons is magnified since the vaporization yield depends on temperature according to an Arrhenius equation. Thus it is clear that the structural change induced by photons near the indirect band-gap energy is not a thermal effect.

Our major concern in this paper is the dip in the curve of threshold fluence versus photon energy observed at the indirect band-gap photon energies, which corresponds to none of the optical-absorption bands in pure GaP. Thus the dip cannot be ascribed to bulk optical absorption. On the other hand, experiments¹³ and theories¹² of electronic structure of the GaP(110) surface show the presence of occupied and empty states near the conduction and valence bands, respectively. The presence of such surface states is expected for any reconstructed structures because of the combination of dangling bonds. It is most conceivable that these surface states are formed near the indirect band gap, at which the density of the states is high and the wave-number selection rule is not effective for the surfaces. A similar dip, further pronounced, has been observed in the wavelength depen-

dence at the desorption yield.⁶ The present experimental result indicates more conclusively that a nonthermal process is effective for structural change of the clean surfaces by electronic excitation on surfaces. The presence of the dip for both structural change and desorption indicates further that they arise from the same origin. The reason the dip is more pronounced for desorption is that a damaged surface that has a high optical absorption coefficient for the indirect band-gap photons is formed during desorption experiments.

The structural change observed in the present experiments may arise either from an irreversible phase change induced by crystal instability under electronic excitation above a certain density or from formation of point defects on surfaces. In the latter case the threshold laser fluence does not have strict meaning but is to be regarded as the boundary laser fluence at which the transformation is observable. If the former is the case, the threshold laser fluence will not depend on the repetition, but the experimental result indicates otherwise. The dependence of the threshold laser fluence on repetition, however, cannot exclude the possibility that the observed structural change is a phase change since the increase in the repetition may increase the detection sensitivity. A relatively large decrease in the threshold laser fluence by repetition for the indirect band-gap photons, which can be ascribed to the optical absorption change, however, is in favor of the defect mechanism. In this case if the number of defects formed on the surface is in proportion to the number of electronic excitations, the threshold laser fluence will be inversely proportional to the number of repetitions. The weak dependence suggests that the number of defects produced is a superlinear function of the laser fluence or the number of excitations if the latter mechanism is effective.¹⁴ A similar superlinear relation has been obtained for the relation between the desorption and the laser fluence. The result that the threshold laser fluence for the indirect band-gap photons is reduced by repetition more significantly than that for the direct band-gap photons is ascribed to the increase in the optical absorption coefficient by the structural change near the surface.

Even though the instability under dense electronic excitation has been suggested by Van Vechten *et al.*¹⁵ and treated theoretically by Van Vechten and by Combescot and Bok,¹⁶ these mechanisms are effective only at dense electronic excitation. In their model it is assumed that the reduction of the "average" bonding strength or softening of TA phonons under dense electronic excitation leads to the structural change and desorption. We suggest that formation of point defects on surfaces, induced by localization of electronic excitation and subsequent instability, leads to structural change. The new mechanism is similar to the defect formation in the bulk of alkali halides. Even though both mechanisms assume weakening of the bonds of electronic excitation or by for-

mation of positive holes, the latter appears more effective in bond weakening, since in the former the contribution of holes in weakening a specific bond is inverse to the fractional concentration, while in the latter a hole weakens a specific bond where localization takes place. It has been argued by Toyozawa¹⁷ that localization of two holes (or electrons) at the same site is feasible if the lattice relaxation energy exceeds the Coulombic repulsion energy between two holes localized on a single site. Under the assumption of two-hole localization the super-linear relation can be explained by the reduction of the Coulombic repulsion due to screening under dense electron-hole plasma.¹⁸

In conclusion, the results of the present investigation indicate clearly that electronic excitation at the surfaces of compound semiconductors causes structural change. The problem is related to fundamental problems of lattice relaxation at the surfaces upon formation of surface excitons at a high density and further theoretical investigation is needed. The present investigation suggests further that excitation spectroscopy for structural change and desorption (measured while only a part of a monolayer is desorbed) will yield the optical absorption spectrum of a surface layer, for which only limited detection technique is available at present.¹⁹ There is a vast literature²⁰ on photoinduced modification of surface structures of metals with adsorbates. The present experiments are concerned with clean solid surfaces, but similar measurements of the wavelength dependence may be of use to elucidate the nature of the electronic state leading to desorption.

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