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TOPICAL REVIEW

Treatment of semiconductor surfaces by laser-induced electronic excitation

Noriaki Itoh¹ and A M Stoneham²¹ 1-7-35 Uenohigashi, Toyonaka, Osaka 560-0013, Japan² Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

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Abstract

We review how semiconductor surfaces can be modified by laser irradiation. We deal solely with phenomena induced by electronic excitation, and compare the processes induced by laser irradiation with those induced by electrons from scanning tunnelling microscope tips. The ejection of host atoms from perfect surface sites, or of hydrogen from hydrogen-terminated surfaces, takes place either by single excitation for high-energy photons or with multiple excitation for low-energy photons, even though the quantum yield for ejection by single excitation is extremely low. The atoms neighbouring defects on surfaces are ejected with higher probabilities than those on perfect sites. There appear to be anti-bonding states, embedded in the continuum, such that excitation to them can induce atomic ejection. When the photon energy is too small, multiple photoexcitation or dense excitation is needed to reach these anti-bonding states. Possible applications of laser surface treatments are discussed.

1. Introduction

Just as the electronic excitation of molecules often modifies the molecular structure, so can the excitation of localized electronic states in solids modify the local atomic structure. Generally, the modification results from atomic processes initiated in the electronic excited state which is reached by the excitation. Such relaxation processes are shown schematically in figure 1. In solids in which electron–lattice coupling is strong, a self-trapped exciton can be relaxed to a defect pair comprising an interstitial and a vacancy at originally perfect lattice sites; this is observed in alkali halides, alkaline-earth oxides and several amorphous materials. Such modification of local atomic structure by electronic excitation is not limited to the bulk of solids but it takes place on surfaces and at interfaces. Thus, along with the development of the method of excitation, electronic excitation is now a potential tool of material modification, as reviewed by Itoh and by Stoneham (2000) and Stoneham and Itoh (2000).

The modification of the surfaces by electronic excitation is of both basic and practical interest. Atoms on surfaces have higher freedom of motion than those in the bulk. Therefore the local lattice modification on surfaces, including ejection of atoms, by electronic excitation

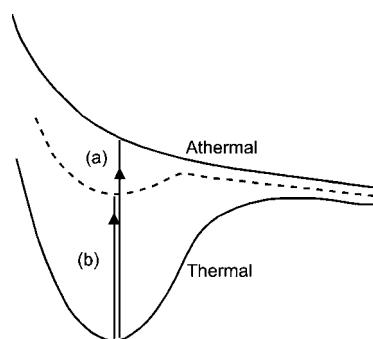


Figure 1. A schematic configuration coordinate diagrams for local lattice modification by electronic excitation. Atomic emission from a surface is one example of this type of process. (a) An athermal process; (b) a thermal process after excitation. If the potential barrier is sufficiently high, case (b) leads to a system in a metastable state on the surface.

takes place with higher efficiencies than the corresponding modification, if any, in the bulk and a variety of local lattice modification that does not appear in the bulk is observed on surfaces. For example, creation of defect pairs in alkali halides from self-trapped excitons in the bulk becomes less efficient as the radius of the negative ion relative to the radius of the positive ion increases. This is not the case for the surfaces: the yield of the ejection of halogen atoms by electronic excitations from surfaces of alkali halides with large negative-to-positive-ion radius ratio is as high as those with small negative-to-positive-ion radius ratio. In semiconductors, in which excitons couple with the lattice less strongly, defects are not created at perfect lattice sites by electronic excitations. However, surface vacancies are generated not only at surface defect sites but also at originally perfect lattice sites of semiconductors by electronic excitation, as we describe in this article.

The sources of electronic excitation of the semiconductor surfaces used frequently are lasers and the electron beams for scanning tunnelling microscopy (STM). Lasers are useful, because of their high intensity, in producing reactions with small quantum efficiency and reactions of which the yields are superlinear functions of the intensity. Lasers with high intensity do not merely heat the surface layers. They can produce lattice instabilities by excitation of electrons in bonding (valence) electrons (bond softening). This occurs when the concentration of electron-hole pairs is around 15% (Graves and Allen 1999). In fact, above about 1.5 times the melt threshold, there is a change in the reflectivity and in the second-harmonic dielectric functions which suggests a solid-liquid phase transformation; this occurs within 1 ps of laser irradiation of Si and GaAs (Sokolowski-Tinten *et al* 1995). Recent measurements of the time-resolved x-ray diffraction of CdTe indicate a loss of long-range order up to 90 nm from the surface on irradiation with 120 fs laser pulses of about 120 mJ cm^{-2} , with time constants as short as 350 fs (Rousse *et al* 2001). Near the melt threshold, the transfer of electronic energy to the lattice causing the change is much slower, and is of the order of the electron-lattice coupling time (0.1–1 ps). In this article, we shall discuss those electronic excitation effects which are more local and which appear at lower laser fluences. Although such high intensities mix thermal and electronic excitation effects, laser beams of moderate intensities make it possible to observe phenomena which are clearly due to electronic excitation, especially those associated with a very specific excited state (Itoh and Stoneham 2000, Stoneham *et al* 1999).

STM is a useful tool for both inducing and characterizing reactions on an atomic scale. Electrons in STM induce atomic processes similar to those caused by lasers. Just as photons

with energy E are selective in inducing excitations of an energy separation E , so do electrons with an energy E induce excitations with energy separation less than E . Given an excitation energy E_T , the cross-section for excitation by electrons has a maximum at 2–3 times E_T . Photons are more appropriate for spectroscopic purposes. The STM is potentially a powerful tool for manipulating individual atoms on surfaces *electronically* as well as through direct forces. Here we shall discuss mainly the electronic excitation aspects of the extraction of atoms.

In this article we survey the local lattice modifications induced by electronic excitation of semiconductor surfaces by STM tips and lasers. Emphasis is placed on the mechanism of material modification by electronic excitation, but we shall also discuss the practical aspects of laser treatments of semiconductor surfaces.

2. Experimental observations

2.1. Removal of host atoms

In table 1, we summarize recent evidence for the ejection of atoms from semiconductor surfaces following electronic excitation by lasers or by electrons from STM tips. We emphasize that *host* atoms, not merely adsorbed atoms, are ejected by electronic excitation. The yield, whether of host or adsorbed species, can show linear or superlinear dependence on beam intensity. Ejection showing a linear dependence is probably induced by a single excitation, as for transition (a) in figure 1. When superlinear dependence is observed, there is no ejection induced by a single excitation (as for transition (b) in figure 1), and further consideration is needed.

Some of the data show a simple linear proportionality of atoms removed to fluence. Chen *et al* (1997) carried out STM observations of the Si(111) 7×7 surfaces irradiated with 6.3 eV lasers, finding that vacancies in the (7×7)-reconstructed structure were generated without disturbing the remaining atoms. The number of removed atoms increased linearly with fluence, with a cross-section of 5.2×10^{-23} cm², independent of temperature from room temperature to 1000 °C. Nakayama and Weaver (1999) and Han *et al* (1999) observed that atoms are removed from GaAs(110), Si(100) 2×1 and Si(111) 7×7 surfaces by 90–2000 eV electron irradiation; again, yields were linear functions of fluence, showing that the removal is due to single excitation. STM observations showed that the creation of vacancies occurred randomly from perfect surface sites, unrelated to existing defects. The cross-sections for atom removal by 100 eV electrons were 4.4×10^{-20} cm² for GaAs(110), 1×10^{-20} cm² for Si(111) and 1.2×10^{-20} cm² for Si(001). Such electron energies are too low to create defects by elastic encounters. Since an electron of 100 eV creates about 30 electron–hole excitations in silicon, the average number of electron–hole pairs per emitted atom is of much the same order of magnitude as with laser irradiation.

In other experiments, similar STM observations of surfaces following irradiation with lower-energy photons also showed atomic emission of electronic origin, but with yields which were superlinear functions of fluence. Ishikawa *et al* (1996) observed vacancy creation on the Si(111) 7×7 surface by irradiation with 2.5 eV laser pulses, while Kanasaki *et al* (1998) used photons between 1.7 and 3.0 eV and showed that the removal rate is enhanced resonantly around 2.0 eV. The removal rate of the centre adatoms of the reconstructed Si(111) 7×7 surface is higher than that for the corner adatoms by a factor of 2.2–3.6. The fluence dependence of the number of atoms emitted at the ground state agrees with that of the number of vacancies generated, and is a superlinear function of fluence. Thus, it appears that a 3 eV photon is not sufficient to induce ejection of a Si atom, yet there is some nonlinear process which seems to induce the ejection. Tanimura and Kanasaki (1999) observed formation of vacancies by irradiation of InP(110) 1×1 surface with 2.7 eV laser pulses, while Han *et al* (1999) stated

Table 1. Observations of the removal of atoms from semiconductor surfaces by electronic excitation. Measurements are made at room temperature unless specified otherwise.

| Surface | Species desorbed | Particles | Energy (eV) | Cross-section (cm ²) | Remarks | Reference |
|----------------------------|------------------|-----------|-------------|----------------------------------|--|------------------------------|
| Si(111)7 × 7 | Si | Photons | 6.3 | 5.2 × 10 ⁻²³ | Linear | Chen <i>et al</i> (1997) |
| Si(111)7 × 7 | Si | Electrons | 90 | 1 × 10 ⁻²⁰ | Linear | Nakayama and Weaver (1999) |
| Si(111)7 × 7 | Si | Electrons | 10 | 7 × 10 ⁻²³ | 30–150 K, linear, the yield drops below 3 eV | Stripe <i>et al</i> (1997) |
| Si(111)7 × 7 | Si | Photons | 1.7–3.0 | | Superlinear, resonant peak at 2.7 eV | Kanasaki <i>et al</i> (1998) |
| Si(001)2 × 1 | Si | Electrons | 2000 | 1.2 × 10 ⁻²⁰ | Linear | Han <i>et al</i> (1999) |
| GaAs(001) | Ga and As | Electrons | 100 | 4.4 × 10 ⁻²⁰ | Linear | Han <i>et al</i> (1999) |
| InP(001) | In and P | Photons | 2.7 | | Superlinear | Tanimura and Kanasaki (1999) |
| Si(001)2 × 1, H terminated | H | Photons | 7.9 | 2.8 × 10 ⁻²¹ | Linear | Vondrak and Zhu (1999) |
| Si(001)2 × 1, H terminated | H | Electrons | > 6.0 | 3.5 × 10 ⁻²¹ | Linear | Avouris <i>et al</i> (1996a) |
| Si(001)2 × 1, H terminated | H | Electrons | < 5.5 | | Superlinear | Avouris <i>et al</i> (1996a) |
| Si(111)1 × 1, H terminated | H | Photons | 7.9 | 1.2 × 10 ⁻²⁰ | Linear | Pusel <i>et al</i> (1998) |
| Si(111)1 × 1, H terminated | H | Electrons | 10 | 8 × 10 ⁻²³ | Linear, threshold at 6.5 eV | Becker <i>et al</i> (1990) |

that 2.3 eV laser beams do not generate vacancies at perfect sites of the GaAs(110) surface. It appears that superlinear excitation processes can generate defects on perfect sites, depending on materials and laser photon energy. Kanasaki *et al* (1999) obtained the same velocity distribution of Si atoms ejected from the Si(111)7 × 7 surface, having a peak at 0.06 eV, for 200 fs and 5 ns laser pulses of several photon energies. The results indicate clearly that the same mechanism is effective for different pulse widths and photon energies.

Scanning probe microscopy tips can remove atoms from surfaces and deposit atoms on surfaces, and may enhance the migration of defects. Three kinds of effect can be distinguished

(see Gauthier (2000) and references therein):

- (1) Interactions due to the close proximity between tips and substances.
- (2) Interactions due to electrical field.
- (3) Interaction due to the tunnelling current from an STM tip.

The tunnelling electrons injected are in a energy range less than 10 eV, and current is 10^{12} electrons per second through an area of atomic dimensions. The current is so high as to induce nonlinear effects, and is also sufficient for detection of reactions with small cross-sections. There are observations of the removal of host atoms from Si(111) (Lyo and Avouris 1991, Uchida *et al* 1993, Huang *et al* 1995, Stripe *et al* 1997) and from Ge(111) surfaces (Becker *et al* 1987, Dujardin *et al* 1998). Stripe *et al* (1997) show that there is a cut-off voltage at about 3 V for the extraction of the centre adatoms of the Si(111) 7×7 surface and that the extraction takes place only when a negative voltage is applied to the tip. The yield, independent of the dose, does not depend on temperature in the temperature range of 30 K to 175 K, which suggests strongly that the extraction of atoms is caused by electronic excitation. The cross-section for excitation by 10 eV electrons is extremely small, only 7×10^{-23} cm², close to the value obtained for photoexcitation. No corner adatoms were extracted in this temperature range. The Si atoms ejected remain on the tip below 175 K but return back to their normal site above this temperature. Thus, earlier work carried out at room temperature, which showed atom removal for both polarities, has been interpreted in terms of the field evaporation. In this case, the centre adatoms of the reconstructed Si(111) 7×7 surfaces are removed at a rate 1.6 times higher than the corner adatoms by STM tips (Uchida *et al* 1993).

2.2. Removal of atoms neighbouring defect sites

The STM data provide evidence that atoms neighbouring defect sites on surfaces are emitted by laser irradiation at higher rates than atoms at perfect surface (terrace) sites. For the Si(111) 7×7 surface, the removal rate of atoms neighbouring a vacancy by 6.3 eV photons is a factor of 10^2 higher than that for those on an undamaged reconstructed surface (Chen *et al* 1997). Han *et al* (1999) showed that the number of pits that extend over several unit cells on GaAs(110) increases as radiation with electrons proceeds, and that the removal yield from the pit boundaries is a factor of 4 higher than that from a terrace. A similar tendency has been seen for Si(001).

Preferential ejection also takes place for low-energy electron or laser beams. Kobayashi *et al* (1994) showed that the dominant extraction by 2.85 eV electrons occurs adjacent to the c-type defects (asymmetrical vacancies; see Zhang *et al* 1996) on the Si(001) 2×1 surfaces. Han *et al* (1999) showed also that 2.3 eV laser pulses create defects on surfaces of GaAs(110) only if the surfaces are already damaged by electron irradiation. Further, preferential ejection of atoms adjacent to vacancies by laser irradiation has been demonstrated for InP(110) (Tanimura and Kanasaki 1999). They showed that 2.7 eV laser beams create vacancy clusters aligned along In–P chains, whereas 2.3 eV laser beams create vacancy clusters extending two-dimensionally (Kanasaki 2001). These results are of interest since they indicate selectivity in generating new vacancies on sites surrounding existing vacancies.

Xu *et al* (1995, 1996) found that a monolayer of Si(100) 2×1 can be removed by 2.3 eV laser irradiation, leaving unreconstructed surfaces resistive to laser irradiation of the same fluence. It would seem that the defective initial surface is removed efficiently, leaving the second surface with fewer defects. Defect-initiated atomic emission of submonolayer sensitivity under laser irradiation of 2–3 eV range, where the yields of the emissions are superlinear functions of fluence, has been studied extensively for surfaces both of silicon and compound semiconductors (Itoh *et al* (1995) and references therein; see also Dubreuil and Gibert (1994) and Vivet *et al*

(1995)). These results show three types of emission, which appear with increasing laser fluence, with respect to the relation between the emission yield and the number of laser pulses irradiated: (1) reduced as irradiation is repeated, (2) remaining constant and (3) increased rapidly to ablation. It appears that the defects that are the source of emission are eliminated in type (1) behaviour, so emission falls with the number of laser pulses. Defects responsible for the type (1) emission were ascribed to adatom-type defects. The defect concentration remains constant in type (2) behaviour; the defects responsible were ascribed to kinks and steps. The defects responsible for type (3) emission, which increases with the number of pulses, were ascribed to surface vacancies.

2.3. Removal of hydrogen from hydrogen-terminated surfaces

Another simple case is the desorption of hydrogen from H-terminated Si surfaces, for which system there is an anti-bonding state for Si–H bond breaking. Avouris *et al* ((1996a); see also Shen and Avouris (1997)) observed hydrogen desorption from the hydrogen-terminated Si(001) 2×1 surfaces caused by electrons from STM tips with energies higher than 6 eV, corresponding to the Si–H σ – σ^* transition. The cross-section of the hydrogen desorption does not depend on the voltage above 6 eV and on the current, and is 3.5×10^{-21} cm². Vondrak and Zhu (1999) have shown that laser-induced excitation of the hydrogen-terminated Si(001) 2×1 surfaces with 7.9 eV photons causes desorption of hydrogen with cross-section 2.8×10^{-21} cm², close to that for excitation with STM electrons. They showed also that the yield is the highest when the incident light which dissociates hydrogen is polarized along the Si–H bond direction.

Pusel *et al* (1998) observed the desorption of hydrogen from the Si(111) surfaces by excitation with 7.9 eV photons, with a cross-section of 1.2×10^{-20} m². Desorption of hydrogen caused by electrons above 6.5 eV from STM tips has been observed for the Si(111) surface with a cross-section of 8×10^{-23} cm² (Becker *et al* 1990). For the Si(111) surface, hydrogen desorption caused by photons appears to be more efficient than that caused by electrons. Vijayalakshmi *et al* (2000) measured the desorption of H⁺ from the Si(001) 2×1 surfaces induced by 6.4 eV laser pulses. The fluence dependence of the yield follows approximately a cubic law, whereas a linear relation is found for electron beams of the same energy range. It is not clear yet whether the difference is one of mechanism or of what is measured, for the number of H⁺ ions emitted is measured for laser beams, but the number of atoms removed is measured for electron beams.

The isotope effect in hydrogen desorption from the hydrogen-terminated Si(001) surface has been observed for STM electrons (Shen *et al* 1995) and for lasers (Vondrak and Zhu 1999). The cross-section for H desorption is larger than that for D desorption by a factor of 50 for STM electrons and of 10 for lasers. These isotope effects have been attributed to the difference in the velocity of the H and D wave packet on the excited-state adiabatic potential energy surface (Avouris *et al* 1996a, Vondrak and Zhu 1999) and to the existence of efficient excitation-quenching channels (Avouris *et al* 1996a). A somewhat similar phenomenon has been observed for the STM patterning of Si(100) 2×1 :H in ultrahigh vacuum (Lyding *et al* 1996a, b). It appears that the tunnelling electrons stimulate H desorption. This is a depassivation mechanism, in that the dangling bond exposed can trap carriers; repassivation is possible with ammonia. There is a strong isotope effect (Lyding 1996a, b) seen in what may be analogous experiments in a field-effect transistor (FET). One H can be removed for every 4×10^5 electrons, whereas one D removed for every 10^8 electrons. This would allow a decrease in the FET channel length, which would give greater advantages than increasing FET lifetime. However, it is not completely clear that the STM and FET cases are equivalent (van de Walle and Jackson 1996).

A superlinear dependence of the desorption yield is also observed for hydrogen desorption

caused by STM electrons and lasers with lower energies. Shen and Avouris (1997) observed that the H-removal yield from the H-terminated Si(001) surface caused by STM electrons is much lower for electrons with energies below 6 eV, and is a superlinear function of current, indicating that multiple excitation is needed to remove hydrogen atoms. Because of the relatively long lifetime of the vibrational excited states of the Si–H system, it has been suggested that vibrational cascade excitation causes the desorption. Pusel and Hess (1999) showed also that the H-removal cross-section for removal from the hydrogen-terminated Si(111) surface by 4 eV laser beams is a superlinear function of fluence. However, here the desorption was ascribed to thermal desorption due to the high optical absorption coefficient at this photon energy. According to Shen and Avouris (1997), irradiation with electrons of the hydrogen-terminated Si(001) surface below the cut-off energy induces H desorption, and is different from thermal desorption, where H molecules are desorbed. For the desorption due to electronic excitation of the hydrogen-terminated Si(111) 3×1 surface, which consists of alternating rows of monohydride and dihydride units, the desorption rate of monohydride is a few times higher than that of dihydride, while thermal desorption from dihalides takes place at a temperature 100 K lower than that from monohalides (Shen and Avouris 1997).

Pusel and Hess (1999) showed that the velocity distributions of hydrogen atoms ejected from hydrogen-saturated Si(111) surfaces by 7.9 and 4 eV laser pulses are different. The velocity distribution at 4 eV fits a Maxwell distribution at 900–1600 K, and increases with fluence. Emission is attributed to heating. The velocity distribution at 7.9 eV fits a Maxwell distribution at 330 K, independent of fluence. It is ascribed to ejection following electronic excitation to an anti-bonding potential energy surface. The velocity distribution of hydrogen atoms ejected from Si(001) surfaces by 7.9 eV photons was fitted to a Maxwellian distribution at 2070 K (Vondrak and Zhu 1999).

2.4. Desorption of halogens from semiconductor surfaces

The processes induced by electronic excitation of halogen-adsorbed semiconductor surfaces are of practical importance, as tools of etching surfaces. For the Si(111) 7×7 surfaces, Cl is known to be adsorbed on each adatom of the (7×7) -reconstructed structure as a monochloride (and Br as a monobromide) at low coverage, whereas a dihalide or a trihalide is formed for coverages near saturation (Boland and Villarubia 1990, Schnell *et al* 1985). Mochiji and Ichikawa (2000a, b) made STM observations of the effects of electron irradiation of Br-adsorbed Si(111) 7×7 surfaces. They found that desorption of Br bonded on Si adatoms takes place at low Br coverages; when coverage is increased to the saturation level, Si adatoms are desorbed along with Br. The threshold energy for desorption of Br seems to be between 10 and 20 eV. It is not clear whether the removal rate is linear or superlinear, but it is probably linear, in view of the high threshold energy. Miyamoto (2001) suggested that Br desorption is induced by creation of a hole on the Br 4s orbital, which is located 15 eV below the top of the valence band. The explanation for silicon desorption is considered to be the presence of multiple bromination at adatoms. Most probably, single excitation of back bonds is responsible for the desorption of Si below 20 eV. The yield was found to increase as the energy crosses the Br M and Si L edges, indicating that the desorption occurs also by the Feibelman–Knotek mechanism, due to creation of two localized holes in the valence band within 10 fs following Auger transitions. Measurements of ions emitted by electron irradiation of Br-adsorbed Si(111) 7×7 surfaces indicate that Br ions dominate for Br coverage less than 0.1 monolayer; while the emissions of SiBr and SiBr₂ ions are observed at higher coverages (Mochiji and Ichikawa 2001).

Similar results have been found for the effects of laser irradiation on Cl-adsorbed Si(111) 7×7 surfaces. STM observations (Suguri *et al* 1993), measurements of emitted

particles (Hattori *et al* 1996) and changes in the photoemission spectra (Iimori *et al* 1998) show that desorption of Cl dominates at low coverages. The desorption of dichlorinated and trichlorinated silicon, but not silicon monochloride, is observed at high coverages. The removal rates are superlinear functions of fluence: there are threshold laser fluences above which the desorption is observed, but they are probably an indication of high superlinearity. There is a dependence on photon energy. The change in STM pattern can be observed for 4.7 eV photons, but not for 3.4 eV photons. The particle emissions and the change in the photoemission spectra take place for photons above 2 eV. Just as for the removal of host atoms and hydrogens, the removal of halogen by electronic excitation appears to take place by a single excitation for high-energy excitations above about 15 eV, but by multiple excitation for lower-energy excitations. Yonezawa *et al* (1994) showed that the threshold energy for Cl⁺ emissions from Cl-adsorbed Si(111)7 × 7 surfaces is 17 eV, close to the excitation energy of electrons from the Cl 3s orbital to the conduction band. The relationship between these primary processes of Si removal on halogen-adsorbed Si surfaces and photoetching in halogen atmosphere, reviewed by Rhodin and Paulsen-Bouz (1997) and Rhodin (1995), is a problem to be explored.

2.5. Change in surface morphology

Several authors have made studies of changes of the morphology of the surfaces of compound semiconductors by irradiation with nanosecond laser pulses at intensities below the melting threshold. The reconstructed structures of GaAs(100), InP(100) (Moisson and Bensussan 1983), GaP(111) (Kumazaki *et al* 1987) and CdTe(100) (Brewer *et al* 1990, 1991) are all converted to a 1 × 1 structure by irradiation with nanosecond laser pulses above a certain threshold. Laser irradiation at higher fluences converts the 1 × 1 structure to an amorphous form and leads to a stoichiometry change. As the fluence increases, this leads finally to laser ablation, with the emission of massive amounts of material. According to the STM observations of Han *et al* (1999), surface defects produced at the initial stage of electron irradiation of GaAs(110) surfaces correspond to single Ga–As vacancy pairs, and stoichiometry is maintained. Thus, the primary stage of the morphology change caused by laser irradiation of a compound semiconductor appears to be generation of vacancy pairs, such that the stoichiometry is maintained. Brewer *et al* (1990, 1991) showed that the stoichiometry of CdTe is maintained for low-intensity laser irradiation, but that surfaces become Cd-rich on irradiation with higher intensities.

Long *et al* (1992) observed a change in surface stoichiometry of the GaAs(110) surface by Auger electron spectroscopy on repeated irradiation with laser pulses of relatively low fluences: scanning electron microscopy shows that Ga islands are formed. Vivet *et al* (1995) observed only preferential ejection of As₂ and formation of Ga islands on the GaAs(100) surface after repeated irradiation with nanosecond laser pulses above a certain threshold fluence, below which only the emissions of which the intensity was reduced as irradiation was repeated were observed. Similar results have been obtained for the InP(001) surface (Dubreuil and Gibert 1994). We may suppose that the stoichiometry change originates in the ejection of surface atoms neighbouring the vacancies which were generated at the initial stage of laser irradiation. It is likely that, for less defective surfaces, the removal of those component atoms more easily ejected by electronic excitations is followed by the removal of another component under gentle irradiation. This may not necessarily be the case under irradiation with intense laser beams. Irradiation with nanosecond laser pulses induces changes in properties, including photoconductivity and photoluminescence, as observed by Raja *et al* (1988) and Gnatyuk (1999, 2000). These results indicate that the properties are closely related to surface defects. Modification of surfaces by electronic excitation is of particular importance for improving the

properties of nanocrystals.

Kwak *et al* (1999) observed that the second-harmonic intensity, measured in reflection from the GaAs(110) surface, is reduced by repeated irradiation with 25 fs laser pulses of fluence in the range of $100 \mu\text{J cm}^{-2}$, about 10^{-3} of those used for inducing nonthermal bulk instability described in section 1. The change in the second harmonic is shown by thermal annealing measurements to originate from surface disorder. Kwak *et al* suggest that the same type of instability as induces the bulk phase transformation can be induced on surfaces with lower hole concentrations ($\sim 2\%$). Comparing particle emissions and surface damage induced by laser pulses in the nanosecond (Nakayama 1983, Ichige *et al* 1988), picosecond (Raff *et al* 1994) and femtosecond ranges, the *apparent* threshold laser fluences are of the order of 100 mJ cm^{-2} , 10 mJ cm^{-2} and $100 \mu\text{J cm}^{-2}$, respectively. Given the nonlinearity of laser-induced processes, the phenomena induced by different pulse widths may originate from the same mechanism.

The treatments of nanocrystals by laser beams will prove to be of practical interest. One interesting problem is whether there is a size effect in generating photodissociation. Orii *et al* (1997) observed the emission of Se dimers caused by laser irradiation of CdSe nanocrystals of sizes of 5–25 nm in diameter suspended in vacuum. According to them, the threshold laser fluence for the dimer emission is smaller by an order of magnitude than that for the emission of neutral particles from the same crystal of large dimensions obtained by Nakayama (1983). The difference may arise from the difference of the method of measurement. Further systematic studies are needed. In semiconductor nanocrystals consisting of less than about 100 atoms, excitons are more likely to be self-trapped (Song *et al* 1996) or trapped by some surface feature; it is possible that ejection of atoms by electronic excitation may be enhanced in these nanocrystals. However, there is at least one complication, in that the structures of small nanocrystals will usually have very high internal electric fields, and these will tend to separate electron and hole, so modifying the descriptions which work well for bulk crystals. On the one hand, the large electric fields may make ion emission easier. On the other hand, recombination will be less efficient for a separated electron and hole pair. When the laser intensity is extremely high, as for irradiation by femtosecond lasers, fragmentation of nanocrystals takes place as observed for Si, probably because of a Coulomb explosion (Bescós *et al* 2000). A further complication for nanocrystals is that they may have problems in losing thermal energy, and relatively high temperatures may be achieved if there is poor thermal contact with the environment. The energy from a single photon of 5 eV can give the atoms of a 100-atom dot an average of 0.05 eV, which corresponds to kT with T of order 550 K.

3. Mechanisms

3.1. Ejection by single excitation

Experimental shows that atomic emissions can be induced by electronic excitation for which the energy of the excitation for emitting an atom exceeds the bandgap energy. We emphasize three points. First, the ejection of atoms is a linear function of the intensity, as observed for the emissions of the constituent atoms from the Si(111), Si(001) and GaAs(001) surfaces and for the emission of hydrogen or halogen from the Si(001) and Si(111) surfaces terminated with hydrogen or halogen. Secondly, the ejection of atoms follows a superlinear function of the intensity in many cases. Thirdly, site selectivity is observed both for linear and superlinear cases.

Given the experimental observation of ejection linear in the intensity, it is likely that there are anti-bonding-type electronic excited states (including holes in bonding states) embedded in the continuum. Relaxation in these states leads to the emission of atoms. Candidate excited

states might have a hole on a bonding orbital of the back bonds of surface atoms, with an electron bound to the hole, although such an excited state has an energy higher than the bandgap energy and consequently will be embedded in the continuum. In fact, the removal of hydrogens from hydrogen-terminated Si surfaces and of halogens from halogen-adsorbed Si surfaces has threshold energies close to the excitation energies of electrons from the bonding orbitals to the conduction band. Avouris *et al* (1996a, b) carried out self-consistent-field calculations and showed that the Si-H Φ - Φ^* excitation produces a local anti-bonding state, leading to the rejection of a hydrogen atom. They argued that the desorption of hydrogen from the hydrogen-terminated Si surface takes place as a result of Φ - Φ^* excitation. Using the isotope effect, Vondrak and Zhu (1999) evaluated the time for a hydrogen atom to be displaced beyond a critical distance ($\sim 6 \text{ \AA}$) on the potential energy surface for the excited state to be about 0.4 fs. Because the anti-bonding state is located in the continuum, the transfer of an atom on an anti-bonding potential energy surface, leading to ejection, should compete with the delocalization of the hole by electronic interactions in the valence bands. The low quantum efficiency for the emissions can be ascribed to the short hole lifetime against delocalization. For unterminated surfaces, no definite conclusion can be drawn until further studies are made. However, it is plausible that excitons comprising a hole on a surface back bond and an electron in the conduction band relax to an anti-bonding state leading to atomic emission.

Miyamoto and Sugino (2000) used density functional theory with the local density approximation and generalized gradient corrections in calculating the lifetime of a hole in the bonding orbital to be 10 fs before delocalization by interaction with the valence band. According to their calculation, desorption of hydrogen does not take place within this hole lifetime. This result cannot exclude entirely the possibility that the removal of a hydrogen atom takes place as a result of the excitation, given the observed small cross-sections or low quantum yields for the ejection. Miyamoto (2001) carried out similar calculations for Br-adsorbed Si surfaces, and found that Br is not desorbed when an electron in the Br 4p orbital is excited to the conduction band, but a Br atom is desorbed when a hole is produced in the Br 4s orbital. This implies either a key role for the electron in the conduction band or some dependence on the overall charge state in their model. They attributed the result to an increase in the anti-bonding component. It is rather surprising that the presence of a hole in the core orbital alone leads to ejection of an atom. Many of the local lattice modifications in solids by electronic excitation take place by virtue of the electronic excitation energy, but very few are observed to occur by creation of a hole (Itoh and Stoneham 2000).

3.2. Ejection by multiple excitation

Several mechanisms have been suggested in the past to explain the superlinear emissions, as reviewed by Itoh and Stoneham (2000) and Itoh *et al* (1995, 1999). One class of mechanisms assumes the existence of the anti-bonding states embedded in the continuum, while a second class assumes two-hole localization by the negative- U interaction, as suggested by Anderson (1975). Gadzuk (1991) has suggested that incoming photons excite free carriers successively into an anti-bonding state. The excitation to the anti-bonding state competes with the de-excitation of electrons by phonon scattering, for which the time constant is of the order of a few tenths of a picosecond, and therefore applies more to laser pulses shorter than a picosecond (Misewich *et al* 1992).

Hattori *et al* (1992) suggested that a defect-related anti-bonding state can be reached by a series of cascade electronic excitations to intermediate states, with relaxation after each excitation step. According to Hattori's mechanism, the first single-photon excitation creates a hole in a back bond associated with a surface defect, followed by lattice relaxation to a

metastable state (corresponding to transition (b) in figure 1 for a relatively high barrier). Although an emission of an atom is not induced from this intermediate metastable state, it can be excited again by an incoming photon within its lifetime. This lifetime will be relatively short because of its interaction with valence electrons. If ejection of an atom is not induced by the second excitation, further excitations are needed to reach an anti-bonding state. Because of strong coupling of each excited state with phonons, each optical transition has a broad absorption band, and consequently a series of excitations may be feasible within a laser pulse of a single photon energy. Two cases where this model might be applied to the emissions from perfect sites are these: (1) the relaxed Si(111)7 × 7 surface, where the distorted structure might produce localized states, and (2) the surface, where the coupling of the first excited state with the lattice is so strong that the relaxed excited state emerges out from the continuum. The presence of a resonant transition that enhances the superlinear emission from the Si(111)7 × 7 surface (Kanasaki *et al* 1998) suggests that the existence of an intermediate transition assists in reaching the anti-bonding state, at least for the first excitation. Cascade excitation may bring the system to the same anti-bonding state as the one that can be reached by single-photon excitation. It is also likely that cascade excitation creates another hole in the proximity of an [e, h] excited state, where the hole is located in a back bond, forming a [2e, 2h] excited state. If two holes are on a bonding orbital, such an excited state will have anti-bonding nature, and can be a candidate for the source for atomic emissions under laser irradiation.

Another class of mechanism assumes a local instability induced by dense electron-hole pairs created near the surface. The processes induced by this mechanism will be enhanced when the thickness of the samples is less than the penetration depth of photons. Itoh *et al* (1985) and Sumi (1991) suggested that the two-hole localization by the negative- U interaction induces local instability, resulting in atomic emissions. Two-hole localization by the negative- U interaction takes place in a time range of 1–10 ps via the interaction with the lattice. It requires that the lattice-relaxation energy exceeds the Coulomb repulsion energy between two holes, which should be overcome for two-hole localization. Thus, Sumi (1991) suggested that the concentration of electron-hole pairs should be sufficiently high that a substantial fraction of charge carriers in the bands have kinetic energies higher than the Coulomb repulsion energy. The density of states near the top of the valence band of Si is ~ 0.1 states eV⁻¹/atom, implying 10% e-h pairs are needed to impart 1 eV/atom on average, which is similar to the conditions giving the bulk instability discussed in section 1. The presence of two localized holes in semiconductors implies that two electrons are bound by these two holes forming a [2e, 2h] excited state. Such an excited state can be an anti-bonding state leading to emission of atoms. Therefore the question is whether the anti-bonding state can be reached more efficiently under laser irradiation by cascade excitation or by accumulation of holes in valence bands. Panchratov and Scheffler (1995) used density functional theory to show that atomic emissions are induced from the GaAs(110) surface when the density of excitons near surfaces becomes high. According to their calculations, when two excitons are produced in a slab of GaAs having a (110) surface, the energetically optimal density distribution corresponds to a double-exciton complex [2e, 2h], localized on a Ga atom, substantially displaced from the surface. The calculation may be a demonstration that atomic emissions can be induced by [2e, 2h] localization from semiconductor surfaces but the critical concentration of excitons required to produce [2e, 2h] localization is not known yet. The negative- U mechanisms clearly lead to some challenging theory which is still only incompletely addressed.

So far we have considered instability in electronically excited states or in two-hole localized states. Another approach to defect processes induced by electronic excitation is local heating or phonon kicking, which is often used for describing radiation-enhanced diffusion in semiconductors (Stoneham (1981) and chapter 7 of Itoh and Stoneham (2000)). In this

approach, it is assumed that electronic excitation energy is converted to phonons, raising local temperature, with the result that thermal motion needs to supply only a part of the energy for the defect reaction. Strekalov (1986) used this approach to evaluate the rate of atomic ejection from surfaces by the recombination of electron-hole pairs. Because of its simple analytical form, Strekalov theory has been used to explain experimental results (Vivet *et al* 1995). Chapter 7 of Itoh and Stoneham (2000) reviews this mechanism. In the simple form just outlined, the rate for the process should show *non*-Arrhenius behaviour. In essence, a rate proportional to $\exp(-E_A/kT)$ would change to $\exp(-E_A/[kT+X])$, where X is a contribution from the excitation. In some circumstances, the activation energy itself can be changed, e.g., if the excitation causes motions which modify the barrier itself.

The roles of surface defects for the enhancement of the laser-induced atomic emissions from semiconductor surfaces are twofold. First, atoms adjacent to defects are less strongly bound and so have a higher probability of being emitted after electronic excitation. Simple descriptions in terms of counting bonds are very incomplete, but they do describe a broadly correct trend. Second, the defects serve as localization sites for electronic excitation energy, reducing the probability for tunnelling to the valence band and producing intermediate states for cascade excitation or localization of another hole.

The mechanism of ejection by multiple excitation is still controversial. Instead of cascade electronic excitations, Shen and Avouris (1997) suggested that cascade vibrational excitations induce the emission of hydrogen from hydrogen-terminated Si surfaces, for which the lifetime of vibrational excited states is relatively long. Stockbro *et al* (1998) suggest that desorption of hydrogen from the Si(001) surfaces under negative sample bias is due to vibrational excitation due to inelastic scattering of tunnelling electrons with the Si-H 5σ hole resonance (see also Stockbro 1999). This explains the power-law dependence on current. It also explains the maximum desorption rate found at 7 V as corresponding to the maximum fraction of inelastically scattered electrons at the onset of the field-emission regime. The enhancement of the motion of anion and cation vacancies on the GaAs(100) surface when an STM tip is applied has been interpreted in terms of radiation-enhanced diffusion, caused by tunnelling of minority carriers to defect levels followed by recombination (Lengel *et al* 1996). Kanasaki *et al* (1998, 1999) have used the model of two-hole localization given by Sumi (1991) to explain the fluence dependence of the yield, yet the presence of the resonance peak for the ejection suggests that at least the first excitation involves creation of an [e, h] excited state with a hole in the back bond.

4. Conclusions

If it is possible to cause atomic emission by electronic excitation to a continuum excited state, this opens new possibilities for materials modification by electronic excitation. The energy of the anti-bonding state will depend on whether the atoms are at perfect surface sites or specific defect sites. The sites from which emission occurs might be selected by choosing the right photon energy. Laser beams have many advantages, both because of the resonant transitions and because they can treat a large surface area at one time, unlike atomic manipulation using electrons from STM tips. Thus a laser technique could be used to eliminate specific adatom impurities on surfaces, to modify defect structures, to tailor the area of terraces by ejecting atoms on steps and to eliminate a few defective surface layers to reveal a new, more complete, surface. The tailoring of the surfaces of nanocrystals is important in improving their properties.

Knowledge about the manipulation of semiconductor surfaces by electronic excitation in atomic scale is still scanty. Xu *et al* (1995) have succeeded in eliminating defective surface layers, but there is debris on the newly revealed surfaces. It will be of interest to carry

out spectroscopic studies of the elimination of atoms at perfect sites of various surfaces and also adjacent to specific defects. These studies will not only give further information on the electronic structures of reconstructed surfaces and of defects on surfaces but also will help to develop techniques for producing less defective surfaces and nanocrystals. One of the most interesting situations would be to find conditions (photon energies and fluences) for eliminating atoms on steps without ejecting atoms from perfect sites. This would make it feasible to eliminate whole terraces selectively, to reveal a new, less defective, surface without introducing additional damage on the new surface. Irradiation with photons below the bandgap energy, which is known to induce emissions from semiconductors (Kanasaki *et al* 1993, Okano *et al* 1994), may be useful for this purpose, since these photons are selectively absorbed by surface defects. Laser irradiation of interfaces will also be interesting, because bond breaking at interfaces make induce rebonding and alter interface structures. Here it is also interesting to use photons below gap energies, transmitting through the bulk and being absorbed at the interfaces: so far, mainly studies with photons above bandgap energies have been carried out (Vivet *et al* 1997).

We have said little about quantum dots, whether the self-organized structures (small enough to show the Coulomb blockade) or the still smaller ones, for which confinement shifts the exciton energies significantly. In the case of the polar dots, such as CdS, the dots will almost certainly have large electric fields at their surfaces. It is hard to identify any small dot structures with a small net charge which largely eliminate these fields. These dots may be in good thermal contact with their substrate or their environment, and may lack good mechanisms for getting rid of thermal energy. If an exciton is created, and it recombines, there will be nearly a bandgap of thermal energy (a few eV), so the dot may be 'hot' for long enough to change its response to a second excitation event. The change of a dot's charge state, perhaps by electron emission, will also change its response to subsequent excitations.

There are many gaps in our understanding of the nature of anti-bonding states reached by single and multiple excitation, and this needs to be explored theoretically. Equally important is the dynamics of such states embedded in the continuum and the accurate prediction of the relative rates for hole delocalization and lattice relaxation. Understanding phenomena induced by laser radiation of semiconductors is still at an early stage, although the phenomena are of practical and fundamental interest.

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