

## Nonlinear energy-selective nanoscale modifications of materials and dynamics in metals and semiconductors

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Studies of nonlinear, energy-selective material interactions localized at surfaces, heterointerfaces, impurities, and defects in solids are described. Particular reference is made to a new molecular interaction effect caused by transfer of surface energy by low-energy collisions, a new noncontact nonlinear optical method of studying electron and hole dynamics at a heterointerface, and a new approach using a free-electron laser developed at Vanderbilt University to activate hydrogen-passivated dopants in silicon. In each case the unique characteristics of particle and photon beams, optimized for the technology, were used to extend the range of applications of these new energy-selective techniques to solve fundamental and applied problems. © 1999 American Institute of Physics. [S1063-7842(99)01709-2]

### INTRODUCTION

Studies of dynamic processes at surfaces, heterointerfaces, and in the bulk have achieved considerable progress at the end of the second millennium following the appearance of new, and technologically more refined, nanosize probes and material processing technologies. This research frequently leads to new physical discoveries and useful applications. In particular in the present paper we report results of research which extends the range of sputtering yield measurements toward very low threshold energies and provides new information on processes of nonlinear energy transfer from molecular and atomic ions to surfaces. We also show that the nondestructive method of optical second-harmonic generation is an important tool for studying Si/SiO<sub>2</sub> heterointerfaces, providing new information on the dynamics of electrons and holes at a heterointerface. Finally, high-intensity, tunable, infrared radiation obtained using the W. M. Keck free-electron laser at Vanderbilt University was used for wavelength-selective excitation of vibrational modes localized at specific impurities and defects. This method offers a fundamentally new approach to resonant nanosize modification of materials, which is important from both the theoretical and practical point of view.

### NEW MOLECULAR INTERACTION EFFECT OBSERVED IN THE SPUTTERING YIELD NEAR THRESHOLD ENERGIES

Measurements of the sputtering yield provide exceptional possibilities for studying the interaction between primary particles and a surface, for example during epitaxial growth or etching. We recently observed a new molecular effect which provides a deeper understanding of processes of energy transfer to a surface at low projectile kinetic energies.<sup>1</sup> A comparison of the sputtering yield per incident atom for low-energy molecular projectiles (such as N<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup>) relative to the corresponding atomic primary particles (N<sup>+</sup> and O<sup>+</sup>) revealed that at energies below the characteristic initial energy of the molecular projectiles, the sputtering

yield per incident atom increases appreciably for incoming molecular ions. Figure 1 gives the sputtering yield per atom for N<sub>2</sub><sup>+</sup> and N<sup>+</sup> ions. All the experiments were carried out in an ultrahigh-vacuum chamber and the sputtering yield was obtained by measuring the number of incoming ions (from the current at an 80% transmission mesh) and measuring the mass change of a polycrystalline gold sample (using a quartz microbalance).<sup>2</sup> Figure 1 shows that the sputtering yield for N<sub>2</sub><sup>+</sup> increases appreciably at low kinetic energies, being approximately four times higher when the kinetic energy of the projectiles is 50 eV. We attribute this increase to the larger quantity of energy transferred by the molecular projectiles per atom compared with atomic projectiles. Assuming that the collision is entirely inelastic, we can easily show that the maximum energy transferred to the target is considerably higher for molecules of mass 2*m* compared with two atoms each of mass *m* (this value is 1.76 for nitrogen molecules and a gold target). This reasoning only holds for low projectile kinetic energies, when the molecules have sufficient time to

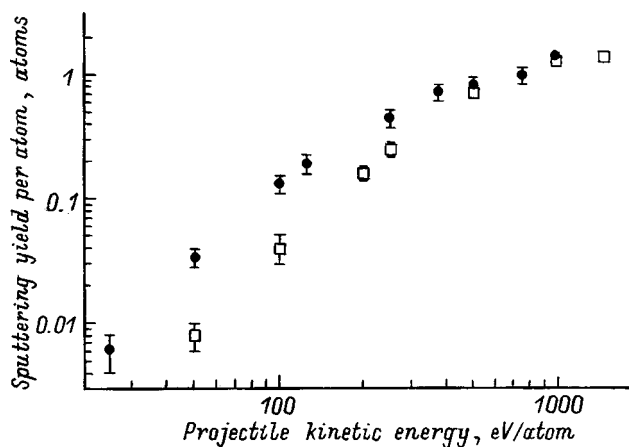


FIG. 1. Sputtering yield per atom for N<sup>+</sup> (□) and N<sub>2</sub><sup>+</sup> (●) ions on a polycrystalline gold target as a function of the primary particle kinetic energy.

interact with the surface. During this collisional interaction time the molecules may undergo several vibrations, whereas at high kinetic energies the collision time becomes so small compared with the period of the vibrations that the molecule interacts with the surface as if it consisted of two separate atoms. Consequently, this new molecular effect is only observed at a specific threshold kinetic energy corresponding to the case when the collision time and the vibrational period are equal. For  $N_2$  (we assume that the ions are neutralized before they impact with the surface) the calculated vibrational period and collision time become equal at a kinetic energy of 224 eV, which shows reasonable agreement with the experimentally observed value of  $\sim 300$  eV. The relationship between these parameters explains why the target "senses" the molecular nature of the diatomic low-energy projectile, whereas at high energy the surface interacts with the molecule as if it consisted of two separate atoms. The importance of the relationship between the collision time and the vibrational period was noted earlier by Landau and Teller to explain the mechanisms of energy transfer by molecular collisions in the gas phase,<sup>3</sup> although this relationship is used here for the first time to explain low-energy molecular scattering processes.

#### CARRIER DYNAMICS AT AN ULTRATHIN OXIDE LAYER-SILICON HETEROINTERFACE

The physical characteristics of the Si/SiO<sub>2</sub> heterointerface have played a vital role in establishing the dominance of silicon in semiconductor technology. As the dimensions of MOS devices continue to decrease, it becomes increasingly important to understand the influence of the thin oxide layer on the carrier dynamics at a buried heterointerface, which may, for instance, lead to breakdown and injection of hot carriers. A recently developed noncontact method of studying dynamic processes at an Si/SiO<sub>2</sub> heterointerface is based on monitoring the second-harmonic generation (SHG) signal. This method can "sense" the electric field (or charge distribution) at a buried heterointerface. All the experiments were carried out using a Ti-sapphire laser with a 150 fs pulse duration; the wavelength was varied between 7100 and 9100 Å, the average power was of the order of 300 W, and the repetition frequency 80 MHz. The beam was focused into a spot of around 10  $\mu\text{m}$  diameter on the sample and the reflected SHG signal was measured using a photomultiplier and a photon counter with a time resolution of 0.5 s.

For all the thermal oxide samples we observed a sharp increase in the SHG signal over the first few hundred seconds of irradiation, followed by gradual saturation. This agrees with the results of observations made by other groups,<sup>4-6</sup> although our results (Fig. 2) also demonstrate a new effect: an appreciable increase in the SHG signal after blocking the exciting beam ( $\lambda = 7900$  Å, maximum intensity 10 GW/cm<sup>2</sup>) for several seconds and then unblocking it. After unblocking the laser beam, the SHG signal dropped rapidly to its saturation level. This characteristic was observed for all oxide layers more than 40 Å thick and at photon energies exceeding the 1.57 eV threshold value.<sup>7</sup> The inset to Fig. 2 shows the SHG signal response for a thin oxide layer

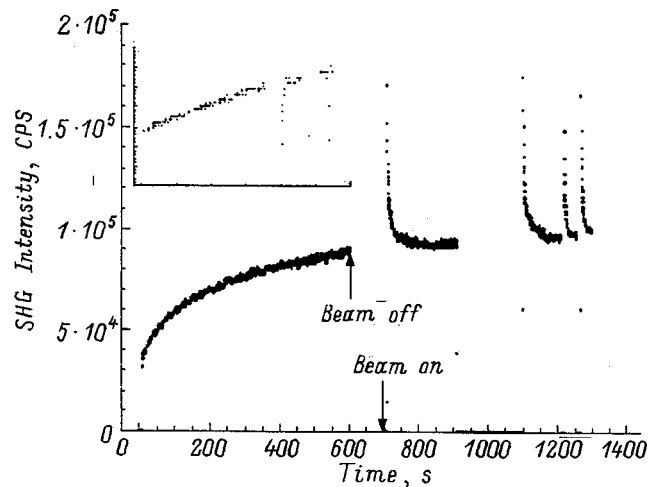


FIG. 2. Time dependence of the SHG signal from a thermal oxide layer 40 Å thick grown on a *p*-type Si(001) substrate. The inset shows the SHG signal after etching the oxide layer to 10 Å.

(around 10 Å), which shows no increase in field as a result of blocking the beam. In this case the field at the heterointerface decreased appreciably.

This effect cannot be attributed merely to multiphoton excitation of electrons in the conduction band of SiO<sub>2</sub> (as has been suggested<sup>4,5</sup> for the initial increase in the SHG signal). We postulate that the holes also play an important role in the charge separation dynamics.<sup>7</sup> In accordance with numerous studies made by other groups the band offset for oxide is between 4.35 and 4.9 eV (Refs. 8 and 9). Bearing in mind that the silicon band gap is 1.1 eV and the SiO<sub>2</sub> band gap is approximately 9 eV at room temperature, and also that the excited beam should have a photon energy higher than 1.52 eV, we conclude that four photons (6.08 eV) are required to create holes in the oxide valence band, whereas three photons of energy exceeding 1.36 eV (4.1 eV) are required to excite electrons from the silicon valence band to the oxide conduction band. Since the transition probability is considerably higher for the three-photon process compared with the four-photon, photoinjection of hot electrons causes an initial increase in the SHG signal although holes excited in the oxide layer also exist. Since the electrons possess a normal mobility of around 0.002 m<sup>2</sup>/(V·s) (Ref. 10), they migrate very rapidly (within a few picoseconds) from the oxide layer, either into the silicon or to the outer surface of the oxide. In contrast the holes possess very low mobility, of the order of 10<sup>-10</sup> m<sup>2</sup>/(V·s) (Ref. 10). Thus, the holes passing through the heterointerface into the oxide will remain in the vicinity. For samples with an oxide layer more than 30 Å thick, holes near or at the heterointerface can easily migrate back into the silicon when the beam is switched off, whereas most of the electrons trapped at the surface remain there. The different behavior of the holes and electrons leads to increased charge separation, which is responsible for the increased dark field in the SHG signal. When the beam is then switched on, the hot holes will migrate across the heterointerface into the oxide, whereas the injection of electrons is severely impeded by the strong space charge field created by the electrons trapped at the SiO<sub>2</sub> outer surface. Conse-

quently, predominantly holes will migrate into the oxide, reducing the SHG signal. For thinner layers of oxide, electrons (like the holes) can tunnel back into the silicon. As a result, no increase in field is observed as a result of switching off the beam. This new effect of increasing field when the beam is switched off, which depends strongly on the oxide thickness and the photon energy, provides a deeper understanding of the role of trapping, generation from traps, and relaxation of holes at the Si/SiO<sub>2</sub> heterointerface, which is extremely important for developing a new generation of microelectronics devices.

### WAVELENGTH-SELECTIVE MODIFICATIONS OF AN *a*-Si-H-P COMPLEX

The W. M. Keck free-electron laser (FEL) at Vanderbilt University is a powerful and unique instrument for studying semiconductors. In particular, it can be used to test the possibility of wavelength-selective modifications of materials. Here we demonstrate its scope for depassivating dopants in hydrogenated semiconductors. The free-electron laser delivers macropulses of 4  $\mu$ s rated duration and energies between 20 and 60 J at a repetition frequency up to 30 Hz; each macropulse consists of approximately 10<sup>4</sup> pulses of 1 ps duration at 350 ps intervals. The FEL wavelength can be tuned continuously in the range 2.0–9.5  $\mu$ m. This range, which is usually increased by frequency multiplication or by using higher harmonics, covers the band-gap energies of most technologically important semiconductors. The high average power and complex time structure of the FEL pulses are used for various spectroscopic studies of semiconductors and for modifying materials. Preliminary work with FELs has already demonstrated that structure-selective modifications can be made to materials.<sup>11–16</sup> The high FEL pulse energy means that energy can be absorbed at specific bonds, leading to localized modifications of materials. These processes depend strongly on the excited-state lifetimes. The intrinsic lifetime, stimulated lifetime, and atomic configuration determine the absorption energy and the suitability of high-intensity infrared radiation for nonthermal wavelength-selective modification of a material.

Hydrogen plays a key role in amorphous silicon, passivating dangling bonds to eliminate defects. However, it also changes the doping properties of *a*-Si-H, binding the dopants and lowering the conductivity. The dopant is passivated by forming a complex with a silicon atom and a hydrogen atom, as shown in Fig. 3. This complex can be seen at 1555 cm<sup>-1</sup> in the vibrational absorption spectra for phosphorus impurities and at 1875 cm<sup>-1</sup> for boron impurities.<sup>17</sup>

We investigated the possibility of using high-intensity FEL laser radiation for selective activation of dopants in *a*-Si-H. By resonantly exciting the hydrogen doping complex, it is possible to remove the hydrogen, leaving the hydrogen at the sites of dangling bonds. Figure 3 shows vibrational absorption spectra for a phosphorus-doped *a*-Si-H film before and after FEL irradiation at 1555 cm<sup>-1</sup>, which corresponds to the vibrational mode of the Si-H-P complex. It can be clearly seen that after FEL irradiation, the shoulder on the low-energy side of the strong absorption line at

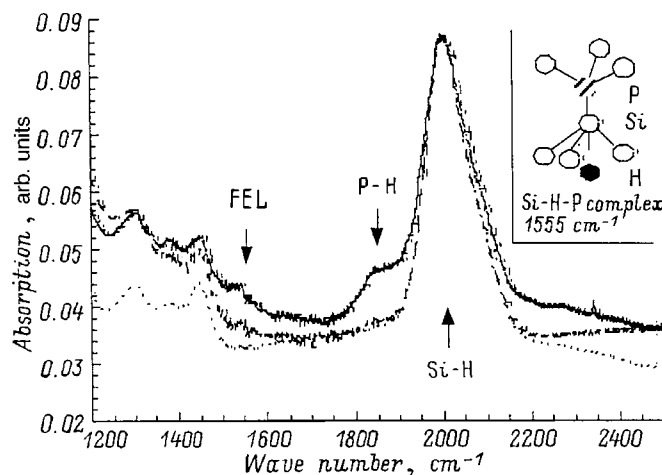


FIG. 3. Comparison between the vibrational absorption spectra before (solid curve) and after FEL irradiation (dotted and dashed curves) at 1555 cm<sup>-1</sup>. The inset shows a schematic of the passivation of donors and acceptors in *n*-type *a*-Si-H.

2000 cm<sup>-1</sup> is reduced appreciably. On comparing the vibrational absorption spectra for *a*-Si-H samples with various dopant concentrations, we find that the intensity of this shoulder correlates with the dopant concentration and we ascribe this resonance to the P-H vibrational mode. Preliminary electrical measurements showed an increase of approximately two orders of magnitude in the surface conductivity of phosphorus-doped *a*-Si-H films, which provides further evidence of the coupling between this mode and the H-passivated donors. It should also be noted that the FEL radiation does not influence the intensity of the Si-H peak at 2000 cm<sup>-1</sup>. These results confirm that dopants could be selectively activated without removing hydrogen from dangling Si-H bonds.

### CONCLUSIONS

We have described three new, fundamental, energy-selective nonlinear effects, relating to the ion-surface interaction, carrier dynamics at an Si/SiO<sub>2</sub> heterointerface, and structure-selective modification of a material. We have observed that energy transfer is considerably greater for molecular ions compared with atomic ions. These results can be used in growth processes, such as molecular beam epitaxy. Second-harmonic generation, applied to study Si/SiO<sub>2</sub> heterointerfaces, has provided a deeper understanding of the nanoscale dynamics of bound electrons and holes, including trapping and generation processes in an ultrathin oxide film. Finally, we have achieved selective activation of dopants which improved the conductivity by two orders of magnitude without removing hydrogen from dangling bonds. This work offers a fundamentally new energy- and site-selective approach which is likely to produce a paradigm shift in the technology of nanodimensional modifications to materials.

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