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# Bombardment-induced light emission from a Si(100) target

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The optical line emission from excited Si atoms following $SF_5^+$ and $Ne^+$ ion bombardment of a Si(100) surface was studied. Transients in the photon yield due to oxygen pressure variation have been observed. The results show evidence of nonlinear sputtering of adsorbed oxygen atoms due to the impact of polyatomic ions. [S0163-1829(97)02420-X]

## I. INTRODUCTION

Ion bombardment of solid targets gives rise to electronic excitation processes that may result in the emission of light from either sputtered or backscattered particles or by the solid itself.[1] The light emission from sputtered atoms and ions has been investigated mostly, so far, by impact of monoatomic projectiles. However, several works have been performed under diatomic molecule bombardment (cf., e.g., Ref. 2), such as $O_2^+$ and $N_2^+$, where radiative deexcitation process in relation to changes of the chemical state of the surface was studied. Quite recently, there has been a growing interest in collision phenomena in solids under impact of polyatomic or cluster projectiles.[3,4] Since the deposited energy density in this case is quite high, nonlinear effects in the collision cascade are expected to occur. This could result in an enhancement of yield values in sputtering-induced phenomena, e.g., secondary ion emission,[5] when compared to that for monoatomic projectiles of the same velocity.

In this paper, we study secondary photon yields from sputtered Si atoms induced by $SF_5^+$ and $Ne^+$ ion bombardment of a Si (100) surface. The $SF_5^+$ molecule was chosen in view of the fact that it represents a cluster of 6 atoms whose average mass is close to Ne. The intensity of optical spectral lines is known to be related to the surface coverage with oxygen. This leads to transient effects, i.e., a variation of the line intensity as a function of time if, for example, the oxygen pressure is suddenly varied. The study of transient phenomena provides information on the sputtering of adsorbed oxygen atoms.

## II. EXPERIMENTAL SETUP

The experiments were performed at the 350-kV ion accelerator of the University of Bielefeld.[6] The Si(100) target was mounted inside a vacuum chamber on an $x$-$y$-$z$ manipulator, permitting also an independent $\phi$ rotation to vary the angle $\phi$ of the target surface normal with respect to the ion beam axis ($z$ axis). Typically, $\phi=45°$ was used during the measurements. The chamber was pumped by a 500-l/s turbomolecular pump down to a base pressure of $2\times10^{-9}$ mbar. High-purity oxygen gas was admitted to the chamber through a pulsed valve and a manual leak valve in series. The pulsed valve provides a gas pulse of 150 $\mu$s duration and can raise the system pressure as high as several $10^{-5}$ mbar within a fraction of a second. Before bombardment, the target was cleaned conventionally by *in situ* ion beam sputtering. The emitted light was collected at 90° with respect to the ion beam by a suprasil lens and focused onto the entrance slit of a 350-mm grating monochromator (GCA/McPherson EU-700) equipped with a grating of 1180 lines/mm and blazed at 2500 Å. The transmitted light was detected with the help of a cooled photomultiplier (Hamamatsu R212) equipped with a S5 photocathode useful for the wavelength region 1850–6000 Å.

## III. RESULTS AND DISCUSSION

A number of authors[7,8] have observed a sudden rise of the light intensity from sputtered excited atoms after the ion beam was interrupted for a certain time interval. In these experiments, the base pressure (typically $10^{-6}$ mbar) was high enough to develop an oxygen coverage on the surface from the residual gases, which is believed to be responsible for the observed change of the line intensity. In the present work, at $\sim10^{-9}$ mbar, no beam-off transient was observed for the Si I 2882-Å line induced by 300-keV $SF_5^+$ ion bombardment if the ion beam was interrupted for several minutes and then was again directed onto the target. This observation indicated that the partial pressure of oxygen was sufficiently low so that the surface remained clean during reasonably short time intervals. However, it was also noticed that several hours of interruption may cause an increase of the light intensity by as much as a factor of 3.5, just after the resumption of the bombardment.[9] In Fig. 1(a), the transient behavior of the Si I 2882-Å atomic line intensity following a sudden elevation of oxygen pressure is presented. After the line intensity had reached an equilibrium value at the high $O_2$ pressure, the oxygen supply as well as the beam were shut off. The bombardment was resumed after the system was back to base pressure. Figure 1(b) shows the decay of the line intensity, which ultimately ended at the original value. It has to be noted that both the rise and the decay time are the same, which reveals that the change of line intensity was caused by adsorbed and not by recoil-implanted oxygen atoms; otherwise, the decay would have been slower. Figure 2 shows how the line intensity varies with oxygen pressure after a small amount of oxygen was introduced into the chamber momentarily. The pressure first rises to about $5\times10^{-5}$ mbar almost instantaneously and then gradually decreases to the base pressure. On the other hand, the line intensity shows an initial increase, passes through a maximum, and then de-

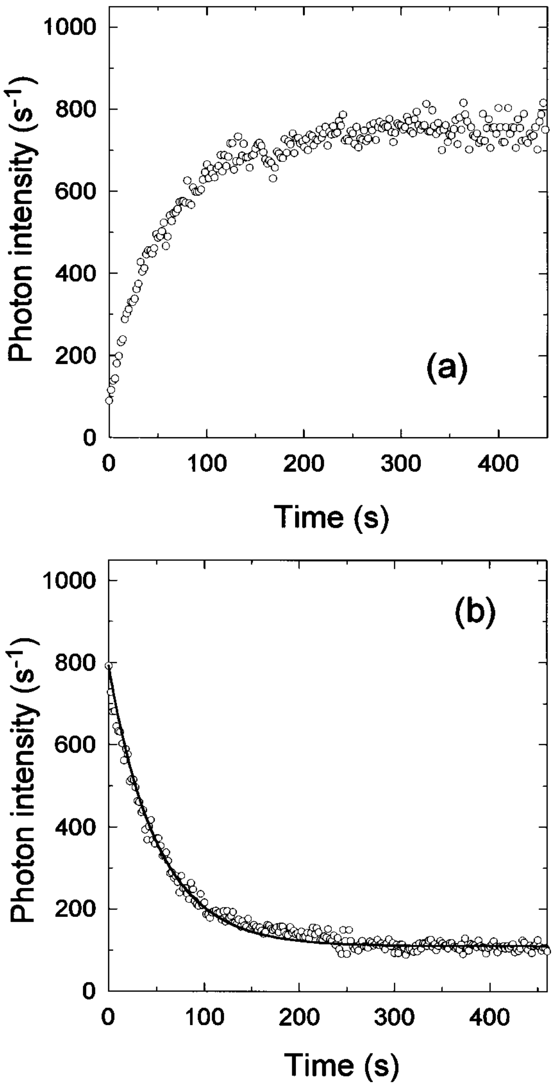

FIG. 1. (a) Transient in the photon yield of the Si I 2882-Å line due to a sudden increase of the partial oxygen pressure to $4\times10^{-5}$ mbar, following 300-keV $SF_5^+$ ion bombardment. (b) Decay of the Si I 2882-Å line intensity following 300-keV $SF_5^+$ ion bombardment of Si surface carrying a layer of adsorbed oxygen. The solid circles are the experimental data points; the solid line represents Eq. (1).

creases exponentially to the initial level. It is interesting to note that there was still a sharp rise in photon intensity at times when the oxygen pressure was rapidly falling down. This is not surprising if one keeps in mind that the degree of oxygen coverage is the consequence of two competing effects: (i) the adsorption of oxygen atoms determined by the oxygen flux density $\Phi_O$ multiplied by the sticking probability $c_s$ and (ii) the removal of oxygen atoms by the incident ion flux $\Phi_i$ multiplied by the sputtering coefficient of oxygen $S_O$. Thus, in the rising part of the photon yield, the rate of adsorption exceeds the rate of erosion. The yield proceeds to a maximum corresponding to an instantaneous equilibrium oxygen coverage, and finally falls down due to both sputtering of oxygen atoms and excessive declination of the rate of adsorption. In terms of these pictures, one can also explain the rather slow increase of line intensity in the rising transient of Fig. 1(a).

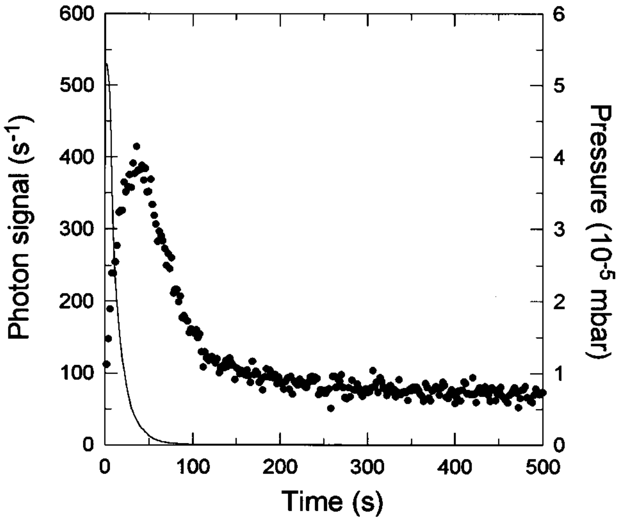

FIG. 2. Transient in the photon yield of the Si I 2882-Å line (●) following 300-keV $SF_5^+$ ion bombardment of Si when a small amount of oxygen gas was introduced into the target chamber by a pulsed valve. The solid line represents the change in oxygen pressure with time.

There is ample evidence that the transients in Si are related to simple oxygen adsorption without any subsequent arrangement or incorporation process.[9,10] In such a case the decay of light yield [Fig. 1(b)] can be described by means of the following expression,[9]

$$I(t)=I_c+(I_O-I_c)\exp\left[-\frac{\Phi_i S_O}{n_s}t\right], \tag{1}$$

where $I_c$ and $I_O$ are the light intensities for a completely clean and a completely oxygen-covered Si surface, respectively, and $n_s$ is the atom density at the surface. A fit of Eq. (1) to the experimental curve yields a value of $S_O\simeq1.83$ atoms per incident molecule for normal incidence angle. Taking further into account that 6 atoms constitute a $SF_5$ molecule, this corresponds to a mean sputtering yield of $1.83/6=0.305$ sputtered atoms per incident atomic particle.

It is well known that the chemical bond of a molecule breaks down upon penetration of the solid target, with the total energy being shared among the constituent atoms. The overlapping of the collision cascades initiated by each energetic particle may lead to nonlinear effects and to spike formation.[11] In order to get evidence of the existence of the nonlinear effect in the oxygen sputtering yield, we have measured $S_O$ for 55-keV $Ne^+$ bombardment; the corresponding projectile energy over mass ratio of 2.75 keV/nucleon was close to the ratio of 2.36 keV/nucleon for 300-keV $SF_5^+$ bombardment. Figure 3 shows the measured transient for the Si I 2882-Å line after the beam was incident onto the Si surface having a layer of adsorbed oxygen atoms. Similar analysis using Eq. (1) yields a value of $S_O\simeq0.12$ atoms/ion for normal ion incidence. Thus, the sputtering yield of adsorbed oxygen atoms per incident atomic projectile in the case of $Ne^+$ ion bombardment is found to be smaller by about a factor of 0.4 as compared to $SF_5^+$ ion bombardment at about the same incident velocity.

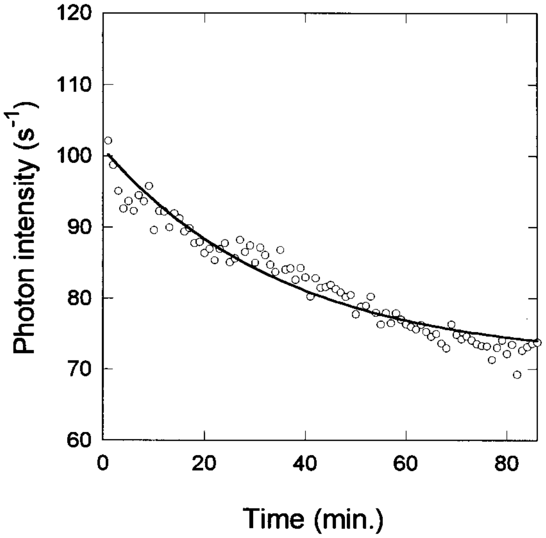

FIG. 3. Light intensity of the Si I 2882-Å line vs time of bombardment when a 55-keV Ne$^+$ beam was incident onto the Si surface carrying a monolayer of adsorbed oxygen. Experimental data points are shown by solid circles; the solid line represents the theoretical curve obtained from Eq. (1).

The mechanisms of ion-induced desorption of a thin layer were discussed by Winters and Sigmund.[12] It was shown that the ejection of an adsorbed atom is the sum of the three contributions due to direct knock-off collisions by the incoming ions, sputtering by reflected primary ions, and sputtering due to momentum transfer from sputtered matrix atoms. At the medium projectile energies of interest here, the first two contributions are small compared to the third contribution. An estimation of this contribution employing the TRIM code[13] for the sputtering of Si matrix atoms by 55-keV Ne$^+$ or 300-keV SF$_5{}^+$ ion bombardment yields a theoretical sputtering yield ratio $6\times S_O^{(\mathrm{Ne}^+)}/S_O^{(\mathrm{SF}_5{}^+)}\simeq 1.05$, which contrasts significantly with the measured ratio of 0.4 only.

An additional sputtering component due to SF$_5{}^+$ ion bombardment may arise from chemical effects (e.g., Ref. 14), i.e., the formation of volatile fluoride molecules at the Si surface by implanted F atoms. Reuter,[15] for example, has studied sputtering of a number of elements including Si under 10-keV CF$_3{}^+$ ion bombardment. From the estimated sputtering yield value and subsequent surface analysis by x-ray photoemission spectroscopy, he concluded that there is physical sputtering of Si by the dissociated atomic fragments. The same conclusion was drawn earlier by Coburn, Winters, and Chuang[16] for etching of Si with 0.05–4-keV CF$_3{}^+$ ions. Andersen and Bay[17] measured normalized sputtering yield of Si for different 45-keV projectile ions including Cl. Their data are also consistent with the collisional sputtering mechanism. In view of the above results and also due to our low beam currents ($\simeq 1.5$ $\mu$A/cm$^2$), it is believed that chemical sputtering is not significant in the present experiment.

In passing, it may be mentioned that chemical effects on the sputtering yield is generally predominant for noble gas ion bombardment in a halogen gas atmosphere (e.g., Ref. 18). Oostra *et al.*[19] noted, however, that for the bombardment of a Si surface at room temperature with simultaneous exposure to SF$_6$, there is practically no chemical reaction largely because of the low sticking coefficient of SF$_6$. In another experiment of Oostra *et al.*[20] the sputtering of Au under I$^+$ and I$_2{}^+$ bombardment, respectively, was investigated. They found a substantial sputtering yield enhancement for iodine dimers compared to the monomer. The results were discussed in terms of a ‘‘collision spike’’ mechanism. Fitting Maxwell-Boltzmann distributions to the energy spectra of sputtered gold atoms, the authors estimated spike temperatures from which it was argued that the surface binding energy is effectively reduced in the case of dimers. The above conclusion was, however, criticized by Szymoński and Postawa[21] who showed that a Maxwell-Boltzmann distribution cannot provide a correct description of the experimental results of Oostra *et al.*[20]

In order to shed some light on the nonlinear sputtering effect observed here, we propose a simple model that is based on the partial overlap of individual collision cascades. For a single atom or ion impinging on a solid surface, the sputtering yield is obtained from the flux of target atoms moving through the solid surface. The energy distribution of the target atoms involved in a collision cascade follows an $E^{-2}$ dependence,[11] with only those atoms that can overcome the surface binding energy $U$ contributing to the atomic sputtering yield $Y^{(1)}$, where

$$Y^{(1)}=C\int_U^\infty E^{-2}dE=C/U, \tag{2}$$

and $C$ a normalization constant. During sputtering with molecular ions, each of the $n$ constituent atoms of the impinging molecule is considered to create a collision cascade. If these collision cascades do not overlap, there will be $n$ unperturbed collision cascades each of which gives rise to a sputtering yield $Y^{(1)}$. For the sake of simplicity we assume here the impinging molecule consists of $n$ identical constituent atoms. The sputtering yield $Y^{(n)}$ per incident molecule in the unperturbed case is just $n$ times that of a single atom,

$$Y^{(n)}=n\times C\int_U^\infty E^{-2}dE=n\times Y^{(1)}. \tag{3}$$

If the collision cascades do overlap, however, the total number of target atoms involved in these cascades will be reduced by, say, a factor $f$ ($f\leqslant 1$), while the mean energy transferred to these atoms will be enhanced by $f^{-1}$. The sputtering yield $Y^{(n)}$ per incident molecule is then obtained as

$$Y^{(n)}=n\times f\times C\int_U^\infty (fE)^{-2}dE=\frac{n}{f}\times Y^{(1)}. \tag{4}$$

Equation (4) predicts a yield that differs by a factor $f^{-1}$ from the no-overlap case [Eq. (3)]. The present experiment suggests that $f=0.4$.

In conclusion, the transient phenomenon in Si is due to a change of the equilibrium oxygen coverage on the surface, which is the consequence of simultaneous adsorption and sputtering of oxygen atoms. An enhancement in the sputtering yield of oxygen atoms by a factor of 2.5 is observed under molecular ($SF_5{}^+$) ion bombardment as compared to atomic ion ($Ne^+$) bombardment at about the same velocity. This nonlinear effect in the sputtering yield is believed not to arise from chemical effects but can be attributed to overlapping of individual collision cascades in the sputtering process.

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