Reneutralization time of surface silicon ions on a field emitter

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Abstract. In this work, the lifetime of silicon (Si) ions generated through photoionization of Si surface atoms from a field emitter was measured. Under low-intensity fs laser pulse illumination, a linear dependence of the number of evaporated ions per pulse on the laser intensity was observed. A simple model was developed to explain this linear dependence and to estimate the rate of success of the field evaporation process. It is shown that the number of evaporated ions per pulse depends on the standing field applied to the Si surface, demonstrating the existence of an ionic energy barrier for Si ions. The lifetime of these ions was estimated to be 0.5 ps.

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Laser interaction with semiconductor surfaces has been studied extensively, motivated both by its applications in materials processing and by basic research on light–matter interaction. Among the materials used widely in micro-industrial applications, silicon attracts special attention owing to its remarkable electrical and optical properties. Based on laser–silicon interaction, changes to surface atomic structures are often induced, and electronic processes have been shown to play an important role in these changes when the laser intensity is below the melt threshold. Adatoms of the $7 \times 7$ structure of a clean Si(111) surface are removed selectively by irradiation with a nanosecond laser in the visible range (Chen et al 1997). It has been shown that Si adatoms are ejected from the surface in the electronic ground state as a direct consequence of the electronic bond breaking of adatoms (Kanasaki et al 1999). The theory developed by Itoh and Nakayama assumes that rupture of a surface bond by two-hole localization leads to ejection of adatoms from the surface due to Coulombic repulsion between the two holes and the lattice relaxation (bond softening and breaking; Itoh et al 1985). The ejection of adatoms is a linear function of the laser intensity only for photon energies larger than the band gap; when the photon energy is almost equal to the band-gap energy, a super-linear behaviour is observed. However, for pulsed laser deposition and nano-materials synthesis, the laser has to remove not only adatoms but also atoms from all of the surface. The theory of Si atom ejection as ions (cation) from a surface is completely different from that of adatom ejection and there is still a debate about the different proposed mechanisms: ultrafast melting, surface structure modification, thermal and non-thermal ablation mechanisms and direct cluster emission (Bulgakova et al 2004, Marine et al 2008).

Laser-assisted atom probe tomography (APT; Blavette et al 1993, Gault et al 2006) can be used as a new experimental setup for testing some of these mechanisms. In APT, surface atoms are removed one by one by field emission from sharp tips with an end radius of about 50 nm subjected to a dc voltage of several kilovolts and a laser pulse. The chemical nature of the evaporated ions is determined by time-of-flight mass spectrometry. A particular advantage of the field evaporation technique lies in its strict surface nature: APT can be used as a highly sensitive instrument for the surface properties. This technique is widely used with excellent results in material science for studying very fine nanostructures in metals and alloys (Blavette and Bostel 1984). The possibility of field evaporating a silicon tip with a femtosecond laser was shown by...
Gilbert et al (2007) a few years ago. The physical process of semiconductor evaporation in APT is still under discussion (Kellogg and Tsong 1980, Tsong and Kinkus 1984, Vella et al 2007).

In the field-free case of flat surfaces, it was proved that when the laser intensity is below the melt threshold, a nonthermal ejection process is possible, supposedly due to Coulombic explosion (Roeterdink et al 2003). However, it has been demonstrated that macroscopic coulombic explosion in silicon is improbable at femtosecond IR laser irradiation (Bulgakova et al 2004). To understand what happens at low laser intensities, we study the ejection mechanism of silicon cations observed in APT at low laser intensities. The nature of potential ionic states is elucidated by supplying an additional electric field.

We observed the photoionization of surface atoms followed by their evaporation and a post-ionization by tunneling near the tip. The observation of this process for silicon at low laser intensities is a major advancement for the application of APT to semiconducting materials. Indeed, at low laser intensities, all thermal processes should be minimized. This is important for avoiding long evaporation times or any degradation of the spatial resolution of three-dimensional (3D) images reconstructed on the atomic scale.

Moreover, in the case of Si surface ablation, the resonant photoionization can explain the nonthermal ejection, taking into account the surface standing field in the selvedge zone.

In addition, we demonstrate the existence of an energy barrier for ionized atoms which induces a typical lifetime of ions on the surface of about 0.5 ps. This result closes the debate concerning the two possible models of field ion evaporation: the image force model and the charge exchange model (Gomer 1951, Miller 1956). The first one assumes the existence of an ionic barrier and a thermal activation of the evaporation. According to the second one, the field is strong enough to eliminate the barrier totally and the evaporation occurs by surface atom excitation.

This paper is organized as follows. In section 1, after a short overview of existing field evaporation models, we discuss the photoionization process and present our calculations on the photoionization probability. In section 2, our experimental results are presented and compared to this new model. In section 4, the conclusions drawn are given.

2. Theoretical considerations

When a positive electric field of several volts per angstrom is applied to a metal surface, surface atoms evaporate in the form of ions. Two basic theories were developed to describe this phenomenon: the image force model (Miller 1956) and the charge exchange model (Gomer 1951, Miller et al 1996). Both are based on simple models of atomic and ionic forces, image potentials and polarization effects. In the absence of an applied field, the desorption energy \( Q_0 \) that is required for removing an atom from the specimen surface as a positive ion of charge state \( n \) is given by

\[
Q_0 = \Lambda + \sum_n I_n - n\varphi_e > 0,
\]

where \( \Lambda \), \( I_n \) and \( \varphi_e \) are, respectively the heat of sublimation, the \( n \)th ionization energy and the work function of the emitting surface. In the presence of an external field, the ionic states become more stable as the distance from the metal surface is increased. Ignoring the ion core
repulsion, the potential energy of the ion can be expressed as

\[ V(x) = -\frac{n^2 e^2}{16\pi \epsilon_0 x} - neFx + \sum_n I_n - n\varphi_e, \tag{2} \]

where \((n^2 e^2)/(16\pi \epsilon_0 x)\) is a simple image potential and \(-neFx\) a field term, with \(x\) being the distance from the image plane (see figure 1). The position of the maximum of the ionic potential curve is given by

\[ x_{\text{max}} = \sqrt{\frac{ne}{16\pi \epsilon_0 F}}. \tag{3} \]

The value of the ionic potential energy at this maximum position is known as the ‘Schottky hump’ and is equal to

\[ V_{\text{max}} = -\frac{n^3 e^3 F}{4\pi \epsilon_0} + \sum_n I_n - n\varphi_e. \tag{4} \]

The activation energy \(Q_n\), i.e. the difference between the atomic and ionic potential energies, is given by

\[ Q_n = -(\Lambda - V_{\text{max}}). \tag{5} \]

The rate constant of the evaporation process is given by the Arrhenius equation,

\[ \phi = \nu \exp\left(-\frac{Q_n}{k_B T}\right) \tag{6} \]

where \(\nu\) is the vibration frequency of surface atoms, \(k_B\) the Boltzmann constant and \(T\) the emitter temperature.

The interaction of a photon with an electron of the surface atom (adatom) could lead to the transition of the electron to a vacant state of the band structure and thus to the ionization of the adatom as proposed by Tsong and Kinkus (1984). The presence of an electric field at the surface induces band-bending; hence the excited state (hole) of the adatoms falls in the band gap of the surface (Tsong 1979, Tsong 1984). The ion lifetime is, hence, long enough to allow the evaporation by a thermally assisted process. The number of absorbed photons at the tip surface is \(N_{\text{abs}}\). If we assume that all of the ionized ions are field evaporated, the number of evaporated ions per pulse is expected to be equal to \(N_{\text{abs}}\). However, according to the image force model, the potential energy of the ion at the Si surface \((V)\), as presented in figure 1, presents an activation barrier \(Q_{\text{ionic}}^n\), as a difference between the minimum and the maximum of the ionic potential energies appears. We can calculate the height of this barrier,

\[ Q_{\text{ionic}}^n = -(V_{\text{min}} - V_{\text{max}}), \tag{7} \]

where \(V_{\text{min}} = -\Lambda + \sum_n I_n - n\varphi_e - ne_{\text{min}}F\) with \(x_{\text{min}}\) being the position of the minimum of the potential energy. In this case, the number of evaporated ions per pulse becomes

\[ \phi = \nu \tau_{\text{life}} \exp\left(-\frac{Q_{\text{ionic}}^n}{k_B T}\right) N_{\text{abs}}^{\text{tip}}. \tag{8} \]

Thus, the effect of the laser pulse is moderated by a field-controlled barrier, which has never been reported before. Our hypothesis is true only if the evaporation process follows the image force model, i.e. only if an ionic barrier exists. Indeed, the charge exchange model regards the field as strong enough to eliminate the barrier totally. The presence of an ionic energy barrier
Figure 1. Potential energy diagram for an atom (grey line) and an ion (black line) in field ionization above a material surface.

means that not all of the ionized atoms will be immediately evaporated. Moreover, the typical lifetime $\tau_{\text{life}}$ of an ionized adatom may be estimated from the experimentally measured number of evaporated ions per pulse,

$$
\tau_{\text{life}} = \tau_0 \exp \left( \frac{Q_n^{\text{ionic}}}{k_B T} \right) \frac{\phi}{N_{\text{abs}}},
$$

where $\tau_0$ is the vibration time of surface atoms, typically a few picoseconds (Kellogg 1984, Rusina et al 2005).

3. Experimental results and discussion

3.1. Experimental setup

Experiments were performed in an atom probe chamber with a flight path of 10 cm. The surface intercepted by the detector ($\gamma$) is approximately 1/10 of the hemispherical emitter’s surface because of the detector’s field of view. The detection efficiency ($q$) is about 50%. The lowest number of evaporated ions per pulse, which can be measured, is about $10^{-6}$ atoms pulse$^{-1}$.

The laser (T-pulse by Amplitude System) delivers pulses at a wavelength of 1030 nm (which corresponds to a photon energy of 1.2 eV) and a half-width of 500 fs. The radius of the laser spot on the tip is $r_{\text{spot}}$ of 25 $\pm$ 5 $\mu$m. The laser works at a repetition rate of 100 kHz. Thanks to a half-wave plate, the linear polarization of the laser is set parallel to the tip axis.

The silicon field emitter tips are prepared by ion milling from a silicon post in a dual-beam scanning electron microscope (SEM) equipped with a focused ion beam (Miller et al 2005). By annular milling, a radius of about 30 nm is achieved. With the help of the SEM, the size of the
apex and the shank angle are determined with an accuracy of 10 nm. The tip temperature was maintained at 80 K.

3.2. Number of evaporated ions per pulse as a function of laser energy

For a fixed laser energy \( E \), the dc field \( F_{dc} \) necessary to field-evaporate ions at a given rate (of about \( 10^{-5} \) ions pulse\(^{-1} \)) was measured and the field reduction (FR) was calculated as follows,

\[
FR(E) = 1 - \frac{F_{dc}(E)}{F_{evap}},
\]

where \( F_{evap} \) is the corresponding dc field for \( E = 0 \) nJ pulse\(^{-1} \). The FR corresponds to the reduction of the dc field due to the presence of the laser to achieve the evaporation. It can actually be considered as a measurement of the laser contribution to the evaporation. For the fixed dc voltage, corresponding to \( FR = 7\% \) at 47 nJ pulse\(^{-1} \), the laser intensity was changed from 20 to 400 nJ pulse\(^{-1} \) and the number of evaporated ions per pulse was measured, as presented in figure 2. The number of detected silicon ions per pulse \( \phi \) is calculated by counting the number of ions per pulse within a mass range from 13.5 to 15.5 amu (accounting for the three Si\(^{2+} \) isotopes). We restricted our study to the range of intensity of \( (0–400) \) nJ pulse\(^{-1} \) because, for higher energy values, the number of evaporated ions per pulse shows an exponential behaviour, as shown in the inset of figure 2.

From the linear behaviour seen in figure 2, we can safely assume that one atom is ionized by the absorption of a single photon. Moreover, we calculate that the probability of two-photon absorption for the pulse energy of 200 nJ is \( 10^{-14} \) times as small as the one-photon absorption probability. The linear behaviour (reported in figure 2) for a photon energy for the range almost equal to the band-gap energy \( (E_{\text{laser}} \simeq E_{\text{gap}}) \) has never been reported before in desorption experiments of surface adatoms. Therefore, we can assume that atoms are evaporated as ions once in the single charged state and then post-ionized near the tip surface \( (\text{Si}^+ \rightarrow \text{Si}^{2+}) \). To check our hypothesis on this post-ionization, the theoretical curves for the probability of post-ionization as a function of the field strength calculated by Kingham (1982) are compared with 

Figure 2. The number of Si\(^{2+} \) ions per pulse \( \phi \) versus laser energy \( E \).
the amount of $\text{Si}^+ = \log\left[\frac{N_{\text{Si}^+}}{N_{\text{Si}^+} + N_{\text{Si}^{2+}}}\right]$ (open circle) and the amount of $\text{Si}^{2+} = \log\left[\frac{N_{\text{Si}^{2+}}}{N_{\text{Si}^+} + N_{\text{Si}^{2+}}}\right]$ (full circle) versus the FR.

our experimental observations. The measurements are based on the ratio between the relative numbers of $\text{Si}^+$ and $\text{Si}^{2+}$ in the mass spectrum.

Keeping the evaporation rate constant, the FR (i.e. the laser intensity) was changed and the different ionization states of silicon were measured. Initially, for a very high FR, the amount of $\text{Si}^+$ observed is higher than that of $\text{Si}^{2+}$. But decreasing the laser energy and, consequently, increasing the standing field, $F_{\text{dc}}$ (see equation 10), the amount of $\text{Si}^{2+}$ increases, while that of $\text{Si}^+$ ions decreases, as shown in figure 3. The crossover, or rather the interception point where both silicon states are observed in equal amounts, is positioned at $\text{FR} = (32 \pm 1)\%$.

From the theoretical curves calculated by Kingham, this cross-point corresponds to a field of $(19 \pm 4)\text{ V nm}^{-1}$ (Kingham 1982). Taking into account the value for the evaporation field reported in the literature ($F_{\text{evap}} = 33\text{ V nm}^{-1}$; Miller et al 1996), from equation (10), we can calculate the cross-point, $F_{\text{dc}} = F_{\text{evap}}(1 - \text{FR}) = (22.5 \pm 1)\text{ V nm}^{-1}$, which is consistent with the value calculated by Kingham. In addition, data reported in figure 2 allow checking whether the number of ionized atoms ($N_{I}$) is equal to the number of evaporated ions ($N_{\text{evap}}$) or whether a limited number of evaporated ions per pulse, given by equation (8), exist. When the photons arrive at the tip, a fraction of them is absorbed. Because only those ions that are generated at the surface can be field evaporated, we consider only photons absorbed on the first angstrom of the surface $a_0 \approx 0.5\text{ Å}$, the typical thickness of the surface layer and the screening distance (Miller et al 1996). This is the minimum thickness that we can assume. The number of absorbed photons at the tip surface is given by

$$N_{\text{abs}}^{\text{tip}} = \alpha a_0 N_{\text{phot}} S_{\text{tip}} S_{\text{laser}}, \quad (11)$$

where $\alpha$ is the absorption coefficient (for silicon the value of $\alpha$ at 77 K is 10 cm$^{-1}$ (Dash 2001)) and $S_{\text{tip}}$ and $S_{\text{laser}}$ are the surface of the tip and the laser spot area on the tip, respectively.

Now, if we assume that all absorption events at the surface lead to evaporation, the fraction of detected ions per pulse can be predicted as $N_{D} = N_{\text{abs}}^{\text{tip}} q \gamma$, taking into account the efficiency of the detector ($q$) and the fraction of tip apex area intercepted by the detector ($\gamma$). $N_{D}$ is estimated...
to be about \((2 \pm 0.7) \times 10^{-3}\). The experimental value can be obtained from figure 2 for the laser energy used for our calculation \((E_{\text{pulse}} = 230 \text{ nJ})\): \(\phi = N_{\text{exp}} = (1 \pm 0.25) \times 10^{-4}\), which is lower than \(N_D\) by at least one order of magnitude.

This clearly demonstrates that, despite being already ionized, some Si ions remain at the surface despite the intense dc field. This low evaporation probability, \(\phi\), is probably due to the presence of an energy barrier \(Q_{n}^{\text{ionic}}\) for ionized atoms, as predicted by equation (8). The height of this barrier is field dependent and can be measured by studying the variation in the number of evaporated ions per pulse as a function of the standing voltage.

3.3. Number of evaporated ions per pulse as a function of standing voltage

To check the presence of a significant ionic energy barrier, the number of evaporated ions per pulse was measured by changing the dc voltage at the tip, for a fixed value of the laser intensity \((E = 25 \text{ nJ})\). Following equation (6), an exponential behaviour of the flux as a function of the activation energy \((Q_n)\) is expected, which is a complex function of the applied field \(F\), as expressed in equation (4). However, we can approximate the behaviour as linear for a 10% change in the field (Block 1992). The application of the dc voltage to the tip surface generates a field \(F = V_{\text{dc}}/\beta r_{\text{tip}}\), where \(\beta\) is the shape factor of the tip. Using the last expression for \(F\) in equation (10), equation (8) becomes

\[
\ln(\phi) = \ln \left(\nu \tau_{\text{life}} N_{\text{abs}}^{\text{tip}}\right) - \frac{Q_{n}^{\text{ionic}}}{k_B T} = \ln \left(\nu \tau_{\text{life}} N_{\text{abs}}^{\text{tip}}\right) - \frac{Q_{0}^{\text{ionic}}}{k_B T} \left(1 - \frac{V_{\text{evap}}}{V_{\text{dc}}/\beta r_{\text{tip}}}\right), \tag{12}
\]

with \(Q_{0}^{\text{ionic}}\) being the ionic barrier height in the absence of electric field and \(V_{\text{evap}}\) the corresponding dc voltage for \(E = 0 \text{nJ pulse}^{-1}\). The increase in the dc voltage and hence in the surface field \(F\) decreases the ionic barrier \(Q_{n}^{\text{ionic}}\). As a result, the number of evaporated ions per pulse increases. In figure 4, we show the observed behaviour of the number of evaporated ions per pulse for a change in the dc field by about 10%. A linear behaviour on the semilog scale is observed for all the experimental points except for the first one due to the lowest detection limit of the APT. From the experimental data, the value of \(Q_{0}^{\text{ionic}}\) can be calculated: \(Q_{0}^{\text{ionic}} = 0.1 \text{ eV}\). For \(V_{\text{dc}} = 3 \text{ KV}\), the FR(E) is about 14.5%, which corresponds to an ionic barrier \(Q_n^{\text{ionic}} = 0.015 \text{ eV}\). From equation (9), using the value of \(\tau_0 = 1 \text{ ps}\), the lifetime of ionized atoms on the surface can be estimated to be \(\tau_{\text{life}} = 0.5 \pm 0.3 \text{ ps}\), i.e. about half of the surface ion vibration time. Hence, the lifetime will depend on the crystallography direction, as the vibration frequency of surface ions.

4. Conclusion

Our results show that for low laser intensities, the field evaporation of Si atoms from a field emitter under ultrashort laser illumination can be explained by a single-photon absorption mechanism. The atoms are first ionized to the 1+ state and then post-ionized near the tip surface, as predicted by the Kingham theory. These results show that an energy barrier is still present in the ionic potential curve, as predicted by the image force evaporation model. This leads to a measured evaporation probability lower than the number of surface ionized atoms. These results close the debate concerning the two possible models of field ion evaporation: the image force model and the charge exchange model.
Figure 4. The number of evaporated ions per pulse ($\phi$) as a function of the standing voltage $V_{dc}$ applied to the Si tip.

Thanks to the measurement of the ionic energy barrier, the duration of the field evaporation can be estimated. Although the photoionization mechanism is a quasi-instantaneous process, the field evaporation takes some time, about 0.5 ps. This time can be estimated as the lifetime of the photoionized Si atoms on the field emitter surface. This new observation of a very short evaporation process might allow significant advancements in experimental and technical aspects of the laser-assisted APT. The resonant photoionization occurs at very low laser energy; hence a non-amplified fs laser could be used for silicon analysis and silicon surface machining in these regimes. Moreover, as the thermal effects are drastically reduced, the unique spatial resolution of the APT is preserved and its chemical sensitivity is improved.

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