

Transient charge carrier distribution at UV-photoexcited SiO₂/Si interfaces

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We used time-resolved pump-probe core level photoemission spectroscopy to study the transient regime of the charge distribution at SiO₂/Si interfaces after photoexcitation with an UV free electron laser. We found that electrons generated in the Si substrate can accumulate at the surface of the oxide layer, strongly affecting the electric field at the interface. For *n*-type silicon, this effect can lead to an enhancement of the curvature of the bands, rather than to the expected flattening due to surface photovoltage. The characteristic decay time of this vacuum transient charging at the surface of the oxide layer depends markedly on its thickness; our results indicate that for about 12-Å oxide thickness, it is comparable to the typical excess carrier recombination time in silicon space charge layers.

The interface space charge layer plays a crucial role in determining the electrical properties of semiconductor junctions. Furthermore, since in most cases the actual operation of a semiconductor device structure involves perturbing its equilibrium (applying a voltage, or a photoexcitation), the nonequilibrium distribution of the carriers in the space charge region is an important factor.¹ Knowing and understanding its temporal evolution is therefore a major issue, considering also the rapidly reducing size and increasing speed of microdevices, where the whole device structure can be thinner than the typical semiconductor space charge layer, and so frequently solicited to be in a transient nonequilibrium regime.

Using an unconventional approach to two-photon time-resolved photoelectron spectroscopy, based on the combined use of a free-electron laser (FEL) and synchrotron radiation

(SR), we recently showed that surface states can strongly affect the transient regime of the nonequilibrium charge distribution in the space charge layer.² More specifically, we found that the interplay of carrier exchange phenomena between the bulk and the surface can make the excess charge behave very differently from the normal decay, which one would predict considering only bulk recombination processes within the space charge layer itself. In fact, photoexcitation generates electron-hole pairs, which causes a surface photovoltage (SPV) related to the temporary separation of negative and positive excess charge within the Si surface space charge region. Normally, taking into account only recombination in the Si substrate, the band flattening related to the SPV lasts for a time of the order of 0.1–1 μs, before the excess carriers recombine.³ Surface recombination can speed up such transient time, increasing the spatial overlap between

positive and negative carriers. Alternatively, it has been proven that the interplay with charge transfer at surface states can also delay or modify the recombination, causing fluctuations in the SPV decay related to a temporary separation between positive and negative charge.²

In the work presented in this paper, we applied the same technique to the study of a prototype semiconductor interface, Si/SiO₂, and found that in this case a similar and even more dramatic effect on the nonequilibrium charge distribution may occur. Nevertheless, in this case the excess electrons created by UV FEL excitation are not conveyed to surface electronic states of the semiconductor itself. Instead, they diffuse, at least in part, into the SiO₂ overlayer and accumulate at its surface, so that the transient negative charge is again kept far away from its positive counterpart, and its interplay with the space charge layer is strongly dependent on the thickness of the oxide layer. For *n*-type Si, this can give particularly visible effects, because the excess negative charge is conveyed more to the surface than the positive one, instead of more into the bulk, causing an apparent inversion of the SPV. Our study enabled us to determine a range of oxide thickness for which the characteristic time of scattering between the SiO₂ surface and the Si space charge layer is comparable to the typical decay time for SPV related to bulk recombination in Si.

The measurements were performed at the Super ACO storage ring in LURE (Orsay, France), combining the use of the UV FEL and of synchrotron radiation emitted from an undulator and dispersed by a plane grating monochromator. The experimental setup and the possibilities of these two-photon experiments have been extensively discussed elsewhere;⁴ their main feature is the perfect, 1:1 synchronization between the FEL pulses (used as pump), and the SR pulses of the photoemission beamline (acting as probe). In this way, each SR pulse probes the system in the same excited state, thus allowing us to readily extend all the advantages of synchrotron radiation photoemission spectroscopy to the study of FEL-excited systems, while keeping a conventional detection scheme. The SR photon energy was chosen at 130 eV, to guarantee maximum surface sensitivity on the Si2*p* core level photoemission signal. The FEL energy, set to 3.5 eV (350 nm), minimizes the penetration depth in Si whilst creating excess photocarriers; in addition, this energy is greater than the conduction band offset (3.3 eV), but smaller than the valence band offset (4.4 eV) at Si/SiO₂ junctions. The measurements were performed in the experimental station of the SU3 high resolution photoemission beamline, where the FEL light was transported via a series of mirrors. An optical delay line made it possible to change the delay between the FEL and the SR pulses between -2 ns and +6 ns, whereas the repetition rate of the pulses was determined by the two-bunch operation of SuperACO, corresponding to a 120-ns period. Consequently, what we will refer to as -1 ns actually means +119 ns delay between pump and probe. Each FEL pulse delivered more than 1 nJ on the sample, corresponding to an average power of 10 mW, over a 5 mm² spot, uniformly illuminating the beamline focus (which is about 1 mm²). The SR flux (about 10¹¹ photons s⁻¹ cm⁻²) is not sufficient to produce any detectable SPV at room temperature.⁵ The temporal resolution of the technique is determined by the duration of the SR pulse during the experi-

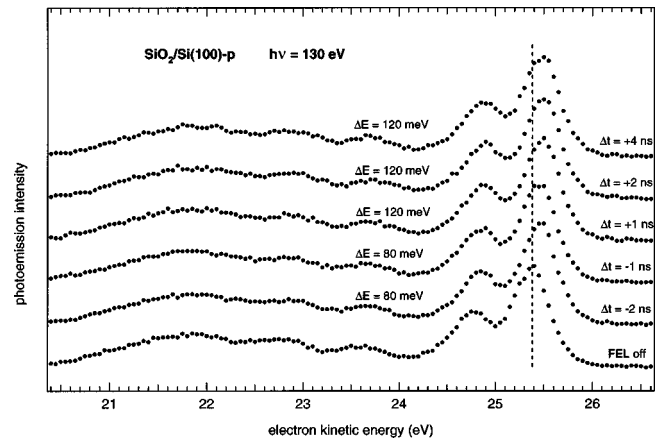


FIG. 1. Effect of FEL irradiation on a 4-Å oxide layer grown on Si(100)-*p*, for various pump-to-probe delays.

ment [typically 300-ps full width at half maximum (FWHM)] whereas the FEL pulse is much shorter (20–40 ps FWHM).⁶

The Si(100) wafers, both of *n* (15–30 Ω cm) and *p* (5–10 Ω cm) type, were prepared following the Shiraki procedure,⁷ leaving a thin, thermally grown oxide layer, prior to introduction in the UHV vessel. Afterwards, the oxide layer was removed with repeated flashes to 1100 C, and ultrathin oxide overlayers were thermally grown *in situ*, exposing the surface to molecular oxygen.⁸ The samples were heated by resistive heating.

Particular care was taken in isolating the surface charge: the electrical contacts were made with Ta clips touching only the back surface of the wafer. The front surface, exposed to the FEL excitation, was in contact only with ceramics (to give a pure mechanical contact), that were carefully covered with a Ta foil to avoid charging effects due to exposure of the ceramic to the FEL or SR photons. In this way, the photoexcited surfaces were grounded only through the Si substrate and the influence of other discharge processes can be ruled out.

We explored the response to the FEL excitation for different SiO₂/Si(100) interfaces. Figure 1 shows the behavior of a 4-Å-thick oxide layer on *p*-type Si(100); as clearly visible from the Si2*p* photoemission peak line shape, all four oxidation states of Si are present,⁸ including SiO₂. Spectra were taken on the photoexcited specimen with different time delays between the FEL pump and the SR probe, and the most representative data points are shown in Fig. 1. Immediately after the FEL excitation, an SPV of 120 mV was measured (+1 ns in Fig. 1). No fluctuations were observed for what we will refer to as positive delays on the ns scale (i.e., for Δ*t* between +0.5 ns and +6 ns): the SPV decays monotonically to 80 mV at negative delays (after 119 ns, -1 ns in Fig. 1). This is a normal behavior for Si, where normal bulk recombination processes cause the recovery of SPV in a time of the order of 100 ns.^{2,3} Similarly, for oxide layers of comparable thickness grown on *n*-type Si(100), an SPV of the same intensity was observed in the opposite direction (with shift of the electronic levels towards higher binding energies) for both positive and negative time delays, again indicating a recovery time for the SPV of the same order of magnitude. For both *n* and *p* type, a cw visible light photo-

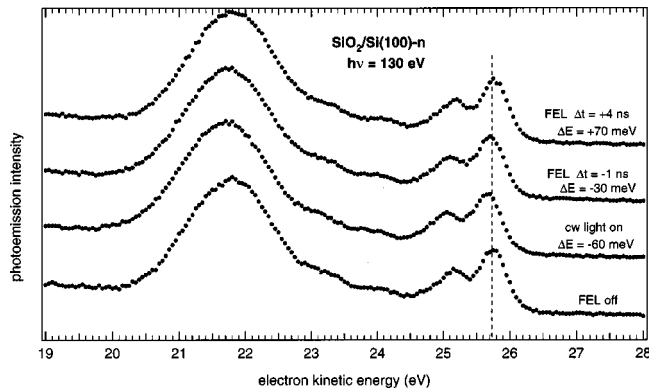


FIG. 2. Shift of the electron energy levels for a 12-Å oxide layer grown on Si(100)-*n*, exposed to FEL and cw visible light excitation.

excitation produces a steady state SPV in the same direction as the FEL. For such ultrathin oxide overlayers, the behavior of *n*- and *p*-type Si is therefore symmetrical with respect to photoexcitation.

Such symmetry is no longer found for thicker oxide overlayers. In particular, *n*-type Si was found to give no detectable FEL induced shift for an oxide thickness of 8 Å. For a thicker oxide layer (approximately 12 Å), such as the one grown on *n*-type Si(100) and presented in Fig. 2, an even more marked difference was found: here, a cw excitation with visible light (sufficient to create an excess of electron-hole pairs in the Si substrate) still causes a shift towards higher binding energies, as one would expect for an *n*-type sample (−60 mV in Fig. 2). On the other hand, a surprising effect takes place with FEL irradiation: for positive time delays the energy levels shift in opposite directions with respect to the cw excitation, (as much as 70 mV, $\Delta t = +4$ ns, as shown in Fig. 2). For negative delays, instead, the shift is the same direction as the cw excitation (−30 mV for $\Delta t = -1$ ns, Fig. 2). No fluctuations of these shifts were observed on the ns time scale for positive delays.

This inversion in band bending dynamics was found to be dependent on doping type and on oxide thickness. In particular, thinner *n*-type samples do not present this effect; conversely, *p*-type samples with an even thicker oxide layer (18 Å, Fig. 3), showed no evidence of inversion, presenting only a monotonic SPV decay (+140 mV at +2 ns, +55 mV at

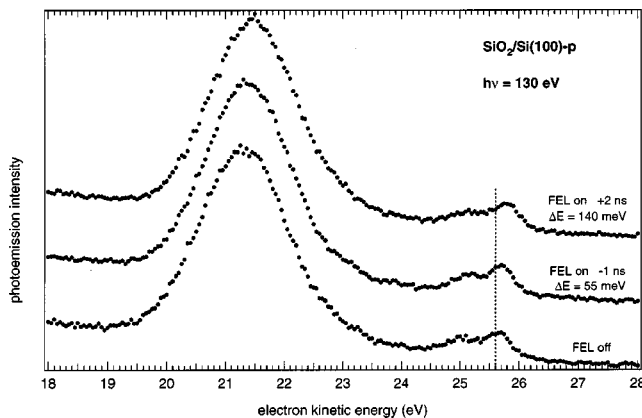


FIG. 3. Effect of FEL irradiation on a 18-Å oxide layer grown on Si(100)-*p*.

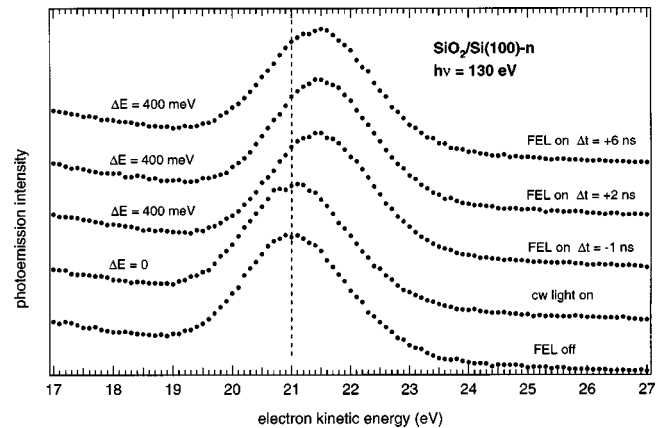


FIG. 4. Shift of the electron energy levels for a thick oxide layer grown on Si(100)-*n*, exposed to FEL and cw visible light excitation.

about −1 ns, in the same direction as the cw excitation).

In Fig. 4 we show instead the results of FEL irradiation on a much thicker native oxide layer (estimated at 40 Å), prepared *ex situ* following the Shiraki procedure and introduced into the analysis vessel. In this case, the shift is consistently in the opposite direction with respect to the expected shift due to SPV, and it shows no dependence on the FEL-SR delay in the 0–120 ns window. Excitation with cw visible light showed no detectable shift of the electron energy levels.

On the basis of the present results, the following conclusions can be drawn: the oxide layer plays an important role in the charge distribution after photoexcitation, and its interplay with the space charge layer in the Si substrate can lead to unexpected effects, especially in the transient regime. Furthermore, the fact that the electric field at the interface depends strongly on the thickness of the oxide layer clearly indicates that this behavior is not determined by interface electronic states. In fact, in that case there should be no variation of the charge distribution for a thickness larger than a few Å. The fact that the “inversion” for *n*-type substrates becomes more relevant with increasing oxide thickness suggests that this is related to electric charge accumulating at the surface of the oxide, which is consistent with previous observations.^{9–11} Furthermore, it should also be emphasized that this transient charging occurs in UHV conditions.¹¹

These experimental results can be readily explained if one assumes that the FEL pulses (3.5 eV), while creating electron-hole pairs in the Si substrate, promote a fraction of the excess electrons from Si to SiO₂, overcoming the 3.3-eV barrier between the two conduction bands. These excess electrons can be created within the same FEL pulse or can be originated by the accumulation of previous excitations. In this way, a fraction of the nonequilibrium excess negative charge moves into the oxide layer and, as already observed elsewhere,^{9,11} migrates towards the surface. The migration process appears to be faster than the time scale of our temporal resolution (0.2 ns). This transient negative charge layer has, of course, two opposite effects on the band bending, according to the substrate doping.

For *p*-type Si, it produces an additional electric field that is in the same direction as the normal SPV. A simple interpretation is to say that a fraction of the excess electrons which normally accumulate in the outermost part of the space charge layer of *p*-type Si move into the oxide: the

transient electric field is always pointing from the excess holes in the bulk (pushed there by the preexisting band bending) to the excess electrons at the surface (directed there by the preexisting band bending in the Si conduction band and by the UV excitation in the oxide layer, respectively).

For *n*-type Si, instead, the fraction of excess electrons which is not photoexcited by the UV light into the oxide layer moves towards the bulk, so that the excess holes are situated in between the two electron clouds. Consequently, for *n*-type Si the negative charge at the surface will produce an electric field acting in the opposite direction with respect to the normal SPV field.

It should be noted that the use of 3.5-eV photons from the FEL gives the electrons the possibility of overcoming the SiO₂/Si conduction band discontinuity,¹¹ whereas it is not sufficient for the holes to cross the valence band discontinuity (4.4 eV). Consequently, no parallel effect due to injection of positive charge into the oxide layer should be expected.¹⁰

The intensity of the electric field related to this negative charge surface layer will be of course proportional to the number of electrons photoexcited into the oxide, and will be also affected by the thickness of the oxide itself (the screening of the oxide is weaker with respect to Si). Anyhow, the main effect of the oxide thickness will be on the lifetime of the transient field, because the recombination of the excess electrons will become slower and slower as a thicker oxide layer keeps them further away from the excess holes in the Si space charge layer. Actually, the key point in the evolution of the transient charge distribution is the interplay between the excess electrons in the oxide and the excess carriers in the Si substrate.

For very thin (few Å) oxide layers, this surface charge appears to be close enough to the Si substrate valence band to cause a very effective “surface” recombination process, which is faster and anyhow adds up to the normal carrier recombination processes. For thicker layers, the overlap between the Si wave functions penetrating into the oxide and the excess electrons becomes poorer, so that the overall recombination becomes slower. In particular, for the intermediate range of oxide coverages (about 12 Å), the surface recombination process appears to take place on a time scale comparable to the characteristic bulk recombination time for Si (of the order of 10–100 ns); the most visible effect of this is that, for instance, we find opposite directions of transient band bending for negative and positive time delays for *n*-type Si. For a thicker coverage, finally, the recombination rate becomes certainly larger than the temporal window accessible by our technique (120 ns). It should be noted that it has been recently ascertained that the leakage current through a Si/SiO₂ gate oxide¹² changes dramatically, by as much as 6–7 orders of magnitude, when the ellipsometric

thickness of the SiO₂ layer changes between 10 and 18 Å, due to the reduced overlap of the evanescent states of Si into SiO₂. Consequently, the 12-Å case presented here fits well in a range of intermediate thickness, where the reduced overlap of interface electronic states reduces the recombination rate between electrons at the oxide surface and the Si substrate. Furthermore, we would like to point out that it corresponds to the thickness which represents the technological limit for silicon dioxide gates [13–15 Å (Ref. 12)], thus providing useful information on the transient behavior of these microdevices.

In conclusion, the nonequilibrium charge distribution at Si/SiO₂ interfaces excited with UV FEL sub-ns pulses, was found to be strongly affected by the oxide layer itself. The experimental data indicate that electrons are injected by the FEL into the oxide, and that they migrate to its surface. This results in a transient separation of at least a part of the excess carriers from the space charge layer region, thus affecting the recombination processes and the band bending dynamics. The effects become particularly evident for *n*-type Si substrates, where the localization of excess electrons at the surface can cause an increase of band bending, rather than the normal flattening induced by SPV. The recombination time for this surface charge is related to the overlap with evanescent Si states decaying into the oxide layer, and consequently depends strongly on the oxide thickness. In particular, it was found that for a thickness of 12 Å, this time is comparable to the characteristic lifetime of the nonequilibrium space charge layer in Si, thus causing fluctuations in direction and intensity of the band bending on the scale of tens of ns. Thicker layers (estimated 20–40 Å) have lifetimes greater than the 120-ns window accessible by our experiment. Thinner layers (5–8 Å) do not produce a detectable shift; in this case, the electrons accumulated at the oxide surface are so close to the Si space charge layer that their role in the recombination process is similar to normal surface defects.

Besides their intrinsic interest for the study of semiconductor junctions, these results can be also especially relevant for all kinds of SPV-based spectroscopies, which are often used to detect and study the role of interface states. In fact, in the case of Si/SiO₂, it should be noted that SPV measurements can be strongly affected by states which are not strictly at the junction, and care should be used in correlating band bending with details of the electronic structure, such as the interface state density.

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