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Photon assisted field electron emission from SiO_2/Si substrates

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We report the observation of a field-emission effect in SiO_2/Si samples assisted by the presence of photons. Electric fields in the oxide of the order of 10 MV/cm^{-1} are attained by photocharging during x-ray illumination and bring the vacuum level to a position below the equilibrium Fermi level. Hot electrons are injected from the Si substrate, traverse the SiO_2 layer, and are emitted directly into vacuum. The large photocharging effect is related to the surface topography, consisting of multiple Si tips of about 1 μm high. *© 1996 American Institute of Physics.* [S0003-6951(96)02925-7]

In this letter we report on the observation of a field-emission effect mediated by the presence of photons. The illumination with x rays of a Si substrate covered with SiO_2 induces a large charge accumulation in the oxide layer which sustains electric fields of the order of 10 MV cm^{-1}. The electric field produces electron injection from the Si substrate into the oxide, acceleration through the oxide and emission into vacuum. The changes of the electronic structure of the system have been monitored by photoemission, allowing the observation of the hot electron spectrum as well. Electron emission through an insulator layer has previously been attained when a thin metal electrode is deposited on the insulator and a bias voltage is applied to it.[1,2] It has also been observed when the metal electrode is replaced by a layer of ions deposited from a corona discharge.[3] However, field emission induced by mere illumination has never, to the best of our knowledge, been reported.

Si(100) wafers, *n* doped with P to 5×10^{17} cm^{-3}, were used as samples. A clean surface showing a (2×1) low-energy electron diffraction pattern was obtained by 1 keV Ar^+ sputtering and ~1200 K annealing cycles. Subsequently, SiO_2 was formed by an oxidation method that yields a rough surface due to simultaneous processes of oxidation (i.e., SiO_2 formation) and etching (i.e., formation and desorption of SiO).[4] Oxidation etching was performed by flowing oxygen through the ultrahigh vacuum (UHV) chamber at a pressure of 1×10^{-5} Torr with a hot tungsten filament opposed to the surface to excite the oxygen molecules while avoiding surface contamination from tungsten oxides. The sample was at ~1200 K and the oxidation time was about 1 h. The topography of the etched surface is composed of SiO_2-covered Si tips with the shape of pyramids resulting from preferential etching of the (100) surface to expose (111) facets. The samples are irregular, comprising thin oxide areas (about 3 nm thick) where no charge is accumulated, and thicker layers (about 30 nm thick) where the charge accumulation and hence the field electron emission takes place. The thickness values are estimated from the photoemission data as explained below. The shape of the tips has been observed by lateral scanning electron microscopy revealing a tip height of ~1 μm and a radius of curvature of the tip ends of about 0.1 μm. Due to the large roughness, the surface of the treated samples is no longer specular. Samples are stable; photon assisted field emission can be reproduced even after air exposed storage for several days without any surface cleaning treatment.

The samples were characterized by x-ray photoemission spectroscopy (XPS) with nonmonochromatic radiation from a Mg anode. The experiments were conducted under UHV conditions and were reproduced in two different systems equipped with hemispherical (Leybold–Heraus) and double pass cylindrical (Perkin–Elmer Physical Electronics) analyzers to check that no artifacts from the analyzer geometry contribute to the measurements of low-energy electrons. Analyzer resolutions of ~150 meV were used, much lower than the spectral width of the x-ray line which is ~750 meV. In this way, the resolution of the photoemission spectra is limited by the spectral width of the $K\alpha$ line, while the structure arising from field emission is limited by the analyzer resolution. Moderate negative voltages are applied to the sample in order to allow the detection of the field emitted electrons. These voltages produce electric fields of 10–100 V cm^{-1} external to the sample, which are amplified at the tip ends with a factor estimated to be between 100 and 1000 according to the tip shape.[5] These field amplification values agree with a typical value of ~200 reported for Si tips formed by controlled etching processes.[6] Anyway, the field at the tip end is under 0.1 MV cm^{-1}, negligible compared with the ~10 MV cm^{-1} required for field emission.

Figure 1 shows an energy distribution curve of emitted electrons comprising the field emission (or hot electron) spectrum and the low-energy side of the photoemission spectrum. Threshold A corresponds to the secondary electron cutoff of flatband SiO_2. Photoelectrons suffering inelastic collisions originate a cascade of secondary electrons that can only escape the solid if their energy is higher than the surface barrier (work function). Cutoff A is the end of the electron distribution curve in a conventional photoemission spectrum. The emission below this edge corresponds to hot electrons injected from the semiconductor substrate into the oxide due to the high electric field. The injected hot electrons are accelerated by the electric field during their motion through the SiO_2 conduction band, undergoing at the same time inelastic scattering processes.[2] As a result, the hot electron distribution curve takes the characteristic shape of secondary electrons with a cutoff B due to the surface barrier of the charged oxide. Secondary electrons originated by photoelectrons can

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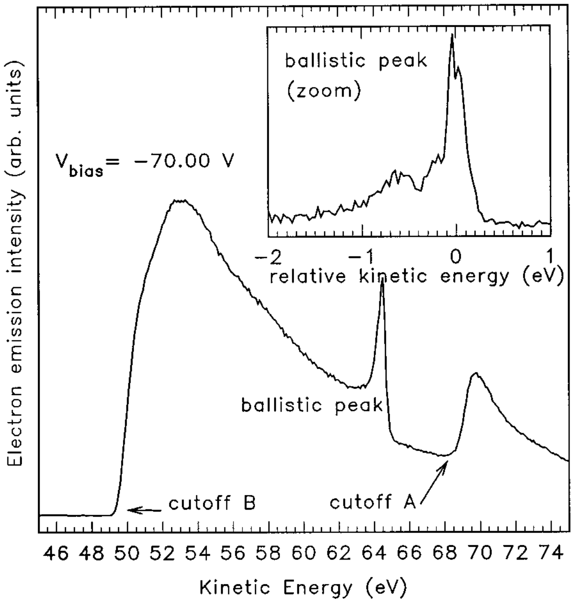

FIG. 1. Low-energy side of the electron energy distribution curve during photoemission measurements showing three characteristic features: the conventional cutoff A, the ballistic peak, and the hot electron cutoff B. Cutoff A corresponds to the electron affinity barrier of flatband SiO_2, and cutoff B to the electron affinity of charged SiO_2. The inset shows a high-resolution spectra of the ballistic peak revealing its narrow shape (~200 meV full width at half maximum) despite the use of nonmonochromatic x rays in the photoemission study, and the presence of other minor peaks on its left side.

also contribute to cutoff B if they reach the charged regions of the oxide before being emitted to vacuum. The separation between cutoffs A and B is the voltage drop across the oxide. A negative bias voltage larger than the separation between cutoffs A and B must be applied to the sample, since the hot electrons are moving in energy levels below the analyzer Fermi level. These hot electrons can escape from the sample because they are not confined by any surface barrier, but some energy must be supplied to them to be detected. The spectrum shown in Fig. 1 was measured with a bias voltage of −70.0 V. The sharp peak located about 4 eV below cutoff A corresponds to electrons traversing the SiO_2 layer ballistically and quasiballistically and being emitted into vacuum. This peak reflects, therefore, the position of the Fermi level in the bulk of the semiconductor, in this case the bottom of the conduction band since the substrate is *n* type. By ballistic electrons we mean those traversing the oxide without inelastic scattering, and by quasiballistic those which have suffered low-energy losses by phonon scattering. A closer view of the peak is shown in the inset of Fig. 1, revealing a structure composed of a main peak with a full width at half maximum of ~200 meV, i.e., roughly the instrumental resolution, and two shoulders on the left side of the ballistic peak at ~0.2 and ~0.6 eV from the main peak. The minor peaks seem related to emission from states of the Si/SiO_2 interface, since they always appear at energies comprised within the Si energy gap. Resonant tunneling through gap states and adsorbate states has been reported as the origin of additional features on field-emission spectra from Si tips.[7]

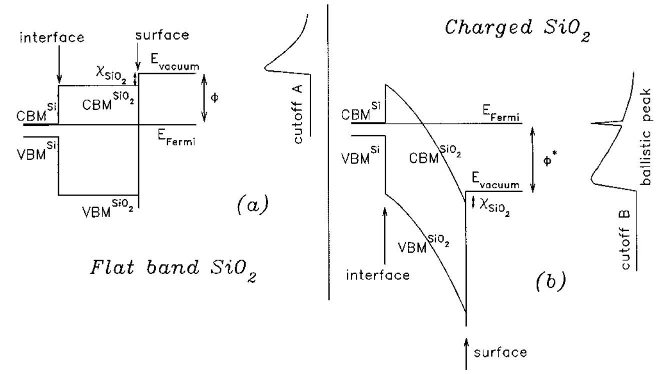

FIG. 2. Band diagram corresponding to the spectrum of Fig. 1, interpreted in terms of two types of SiO_2: (a) flatband oxide, explaining the presence of cutoff A, and (b) charged oxide, yielding cutoff B and the ballistic peak. CMB and VBM are the acronyms for conduction band minimum and valence band maximum, respectively, χ represents the electron affinity and ϕ the work function.

Figure 2 sketches the band structure of flatband SiO_2 and charge SiO_2, and the low-energy side of the electron distribution curve corresponding to each situation. The coexistence of both oxides explains the spectrum shown in Fig. 1. The electronic structure of charged oxide has been represented with parabolic band bending as corresponds to charge located in the whole oxide layer. This charge distribution has been assumed because the charge is induced by x-ray illumination and not by any surface charging technique. Surface charging would yield instead a linear band bending.

Figure 3 shows photoemission spectra of the Si 2*p* and O 1*s* core levels which are consistent with the changes in the electronic structure discussed above. They also allow us the characterization of the sample morphology and the measurement of the voltage drop. From the spectra measured at zero bias (sample grounded) the presence of two oxide phases at the surface is clear: flatband oxide and charged oxide, as no voltage profile in a single oxide layer with a simple charge distribution can account for the presence of two distinct oxide peaks. When the sample is biased, the charge accumulated in the oxide and the voltage drop becomes larger. For large voltage drops, the core level peaks related to charged SiO_2 are broader due to a tail extending to the high kinetic energy side of the spectrum. This tail arises from the convolution of the core level shape with the voltage profile in the charged oxide and the intensity attenuation of buried regions due to the photoelectron escape depth. From simulations of the shape of the charged oxide peaks, the charged oxide thickness is estimated to be 30 nm. The computations are made using the uncharged peaks as reference, an escape depth of 2.5 nm for the Si 2*p* core level, 2.0 nm for the O 1*s*,[8] and a parabolic voltage profile in the oxide, as discussed above. The simulated charged oxide peaks shown with solid curves in Fig. 3 for the O 1*s* spectra are in good agreement. Curves corresponding to thicknesses of 24, 30, and 36 nm are shown, revealing a ~20% accuracy in our estimations. Once the thickness of the charged layer is known, the flatband oxide thickness is estimated to be 3 nm from the intensity ratios (charged oxide/flatband oxide) and (oxide/substrate) in the Si 2*p* and O 1*s* spectra. Thickness values are process dependent and vary for different samples. The magnitude of the electric field in the oxide can be derived from the voltage drop and the oxide thickness. Due to the distribution of charge in the whole oxide, electric fields will be

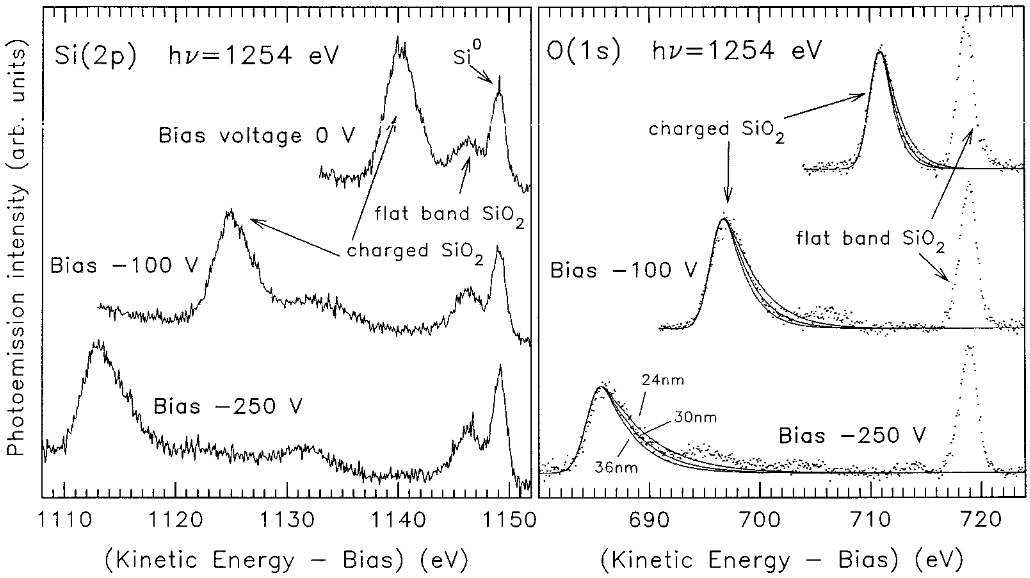

FIG. 3. Photoemission spectra of Si 2*p* and O 1*s* core levels evidencing the presence of two oxide phases at the surface: charged SiO_2 and flatband SiO_2. The charged oxide peaks shift to lower kinetic energies with increasing bias voltage due to the enhancement of photocharging, and are broader due to the convolution of the core level shape with the voltage drop profile. Charged oxide peaks simulated for oxide thicknesses of 24, 30, and 36 nm are shown for the O 1*s* core level, being in good agreement with the experimental spectra.

linear with thickness, reaching a maximum value of 15 and 23 MV cm^{-1} for the spectra of Fig. 3 measured with bias of −100 and −250 V, respectively.

The existence of a voltage across the oxide is due to positive charge accumulation resulting from the balance of photoionization and charge neutralization processes. As the electrons are moving through the charged oxide, some will neutralize the positive charges created by photon irradiation, giving the equilibrium condition for the voltage drop across the oxide. The electrons contributing to positive charge neutralization are those that form cutoff B, i.e., both hot electrons and secondary electrons originated by photoelectrons. For the samples and bias voltages described here the hot electron intensity is always much smaller than the photoelectron intensity (less than 1/100). Accordingly, most of the positive charge neutralization is due to trapping of secondary photoelectrons in the charged regions. The photoelectron intensity has a typical value of 20 nA for the photon flux of 10^{13} photons s^{-1} provided by the Mg anode. Since the sample surface is rough and composed of pyramidal tips, electrons ejected at low angles are captured by the tips instead of reaching the analyzer. When the bias voltage is increased the electrons are preferentially emitted in the forward direction. Therefore the electron flux captured by the pyramids decreases, and the equilibrium condition shifts to larger oxide voltages. Eventually the hot electron emission quenches the increase of the oxide voltage drop, a saturation value of ~70 V for the 30 nm oxide sample described here being obtained. Simple calculations based on this model allow to explain the dependence of the oxide voltage with the applied bias voltage.

In summary, we have reported here the observation of field emission from a SiO_2/Si structure when it is illuminated with x rays. The photons induce charging in the oxide layer, resulting in an electric field strong enough to produce field emission. The large charge accumulation in the oxide is related to the topography of the surface composed of Si tips, since no similar effect has been found in flat SiO_2/Si substrates even for much thicker oxides. The application of an electric field outside the sample without illumination does not produce any field emission. The direct observation of ballistic and hot electrons after traversing the oxide layer may be useful to the study of electron transport through SiO_2 if photon assisted field emission is performed on a regular array of Si tips of controlled shape covered with an oxide layer or if microspectroscopic techniques are used even with irregular samples.

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