Photosensitive Metal–Insulator–Semiconductor Devices with Stepped Insulating Layer

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A preparation procedure based on localized electrochemical oxidation unites multiple metal–insulator–semiconductor (MIS) junctions (also arrays) in a single device. The “stepped MIS” enables a comparative study of several MIS junctions of different oxide thicknesses on one silicon wafer. We present a Si–SiO₂–Au four-step device with oxide thicknesses of 0, 1, 2.5, and 4 nm. The samples are characterized by internal photoemission using variable wavelengths (300–1100 nm). The “1 nm” junction shows an increased photosensitivity compared to the “0 nm” junction (metal–semiconductor system). The internal photoemission drops by 2 orders of magnitude when increasing the oxide thickness from 1 to 4 nm.

Soon after the beginning of the studies on metal–semiconductor (MS) heterosystems, questions regarding the role of an interfacial oxide layer in the conduction properties of the device came up.\(^1\)\(^2\) Provided that the oxide layer is characterized by a large optical bandgap, the electrical conduction can be modeled by quantum mechanical tunneling processes.\(^23\) However, metal–insulator–semiconductor (MIS) devices with an ultrathin oxide layer (\(d < 5 \text{ nm}\)) are especially influenced by interface states at the semiconductor–oxide interface\(^8\)\(^-\)\(^12\) and also midgap states, e.g., oxygen vacancies, which may dramatically change the electrical properties\(^13\) of the devices. Usually, in such devices, the threshold energy (below which no photoemission can be observed) is quite high, e.g., 3–4 eV\(^14\)\(^-\)\(^18\) but it may be reduced by the mentioned interface states.

In this work, we present the experimental approach we employed with the intention to improve the photo- and chemosensitivity\(^19\)\(^-\)\(^20\) of MIS devices rather than to optimize their barrier properties. In particular, we studied the influence of the oxide thickness on the conduction properties of a Au–SiO₂–Si system by preparing an oxide layer of variable thickness on one wafer with a localized electrochemical oxidation procedure (see Fig. 1).

As a measure of the photosensitivity we use the internal photoemission yield (or simply photoyield). It is defined as the net number of electrons detected in the Si electrode per number of photons incident on the Au surface. The individual junctions of the stepped MIS device were characterized by measuring the energy as well as the bias dependence of the photoyield. Using a localized electrochemical oxidation technique, one can increase the photosensitivity of the Si–SiO₂–Au device with respect to the same device with 0 nm oxide thickness (Si–Au device).

The four-step Au–SiO₂–Si structure sketched in Fig. 1 was fabricated on a 20 × 10 mm large piece of an n-type Si(111) wafer (7.5 μm cm). The silicon surface was cleaned with isopropyl alcohol, HF, and Milli-Q water and oxidized in an electrolytic droplet cell\(^21\)\(^-\)\(^23\) using an ammonium acetate buffer electrolyte to minimize parallel corrosion processes during the oxidation.\(^23\) Different areas (typically 0.04 cm²) of the substrate were oxidized with the droplet cell. The desired oxide thicknesses were adjusted by varying the finite potentials (\(E_\text{final} = 2\), 6, and 10 V) of the cyclic voltammograms (CVs).

The different CVs were taken with the initial potential fixed to −1.2 V and a scan rate of 0.1 V/s (reference electrode Ag–AgCl). A stepped silicon oxide layer with steps of about 1, 2.5, and 4 nm oxide thickness and equal area (0.6 cm²) was prepared. Oxidation was performed under illumination of the droplet to provide a sufficient level of minority carrier generation, which is necessary for the oxidation of n-doped silicon surfaces.\(^25\)\(^-\)\(^26\) The value of 0 nm oxide thickness was reached by leaving the HF-treated surface unmodified. As a result, four different junctions were set up on one device in the present work.

The CVs (see Fig. 2) show at around −0.05 V (\(E_\text{C2}, \text{half-wave potential}\)) a considerable current increase followed by a constant value of 150 μA/cm² for the oxidation of an HF-cleaned silicon surface (\(E_\text{final} = 2 \text{ or } 6 \text{ V}\)). When the electrode potential is stopped at \(E_\text{final}\), the current drops exponentially to zero within a few seconds. The oxidation CVs themselves can be used as a tool to check the homogeneity of the oxide. This is demonstrated by setting the droplet on the intersection of previously prepared 0, 1, and 2 V thick oxide layers and by applying a CV with \(E_\text{final} = 10 \text{ V}\). One can clearly see that all previously prepared thicknesses give a special shoulder in the CV (Fig. 2). Silanol formation\(^26\) could not be observed in the CVs on n-type Si.

The calibration of the oxide thickness was performed by ellipsometry and X-ray photoelectron spectroscopy sputter profiles. Film formation factors of 0.4 nm/V for the 6 and 10 V oxide and 0.5 nm/V for the 2 V oxide were found (in agreement with Ref. 27). On top of the oxide, a gold film of 20 × 4 mm was thermally evaporated in high vacuum (base pressure <5 × 10⁻³ mbar) at a low rate (0.3 nm/min) to ensure a homogeneous film thickness.\(^23\) The gold film was contacted at the thicker oxide side to avoid short circuits (see Fig. 1).

As a light source we employed a Xe lamp in connection with a monochromator, which produces a monochromatic beam of radiation with a selectable wavelength in the range between 300 and 1100 nm (photon energies between 1.1 and 4.1 eV). The line broadening of the beam was about 5 nm. The flux of photons impinging on the gold surface was calibrated by employing a silicon photodiode of known sensitivity. The internal photoemission current was measured by means of a potentiostat.

In the following, the internal photoemission current is counted positive if a net electron current is flowing from Au to Si. The sign convention holds for the internal photoemission yield. The bias voltage is positive when the Au top electrode is positively biased with respect to the Si back electrode. This is the conventional forward bias direction for an n-doped semiconductor–oxide–metal system.

In Fig. 3, the internal photoemission yield, induced in each of the four junctions of the MIS device, is plotted on a logarithmic scale as a function of the wavelength of the incident light. The most remarkable observation is that the “1 nm” MIS junction not only exhibits the same broadband photosensitivity as the “0 nm” (MS) junction, but is also a factor of 10 more photosensitive. So yields of \(10^{-6} \text{–} 10^{-5}\) are measured on the 1 nm junction, but only \(10^{-7} \text{–} 10^{-6}\) on the 0 nm junction. Apparently, the oxide layer does not provide, as expected for an insulator, an additional potential barrier to the Schottky barrier present in the MS junction, but leads, on the contrary, to a decrease of the effective barrier “felt” by the electrons excited in the Au layer. This behavior may be explained by the
existence of interface states and positively charged oxygen vacancies in the electrochemically formed oxide layer. In this case, the oxide rather exhibits the behavior of a p-type semiconductor, while the Si–SiO₂ structure may be viewed as an n–p junction. As a consequence, the transport of electrons from Au into Si is facilitated by the presence of the built-in electric field in the p–n junctions.

With increasing oxide thickness, the smooth wavelength dependence is seen to persist only up to about 900 and 800 nm for the 2.5 and 4 nm junctions, respectively. At greater wavelengths, the yield drops drastically, becoming negative at about 1000 and 900 nm, respectively. This indicates that with increasing oxide thickness, a potential barrier for electrons develops in the oxide layer, which cannot be overcome by low energy electrons (< 1.2 eV). As a result, the internal emission is dominated by holes (minority carriers) flowing from Au into Si or electrons flowing from Si to Au, with the net yield dropping down to \( n = 1 \times 10^{-4} \). In addition, the absolute yields measured on the 2.5 nm junction are observed to decrease by about 2 orders of magnitude, while on the 4 nm junction, even by 3 orders of magnitude, with respect to the 1 nm junction (inset of Fig. 3).

The extra barrier introduced by the thicker oxides can be counterbalanced, however, by applying a negative bias voltage to the Au electrode. As shown in Fig. 4, −0.5 eV is already sufficient to extend the broadband sensitivity region of the 2.5 nm junction up to (at least) 1100 nm. In addition, negative biases increase the absolute value of the yields to \( 10^{-2}–10^0 \).

Comparative conductivity–voltage measurements on our devices show small values for negative biases and a strong increase for positive biases similar to previous works. This means that the increase in the photoyield for negative biases is clearly observed in the reverse voltage direction for all junctions. These bias dependences of the photoyield were also reproduced on samples with uniform oxide thicknesses.

In conclusion, we presented an experimental approach based on localized electrochemical oxidation for the fabrication of MIS devices. This procedure allows the production of several MIS junctions of different oxide thicknesses on a single silicon substrate, enabling in the future also the production of junction arrays. The different junctions corresponding to each step of the underlying oxide layer were investigated separately by internal photoemission. The MIS devices show a maximum (at around 1 nm oxide thickness) in the photoemission yield when scaling the oxide thickness from 0 to 4 nm, similar to Ref. 9. Experiments with a greater variety of final values of the CVs will allow further optimization of the

**Figure 1.** (Color online) Schematic setup of the Au–SiO₂–nSi(111) device with a stepped oxide layer.

**Figure 2.** (Color online) CVs of silicon with the specified finite potentials on different areas of the device \( E_{\text{final}} = -1.2 \text{ V} \); \( E_{\text{final}} = 2, 6, \) and 10 V; \( dE/dt = 0.1 \text{ V/s} \). The 10 V CV was taken on the intersection of previously prepared 0, 1, and 2 V oxide layers.

**Figure 3.** (Color online) Logarithmic plot of the internal photoemission yield as a function of the wavelength of the incident light as determined for the four junctions of the MIS device sketched in Fig. 1. The inset shows the photoemission yield at 635 nm as a function of the oxide thickness. All data were taken at 0 V bias.

**Figure 4.** (Color online) Internal photoemission yield as a function of wavelength, plotted for selected negative bias voltages, as measured on the 2.5 nm step of the MIS device sketched in Fig. 1.
device photosensitivities. The broadband sensitivity is probably due to a broad distribution of states across the gap as discussed in Ref. 28. A detailed investigation regarding the energy levels of such states will be done on equally prepared devices with uniform oxide thickness, by means of capacitance–voltage and current–voltage measurements, in a later work. The localized investigation of internal photoemission presented here is also applicable to MIS devices with stepped oxide layers accomplished by other methods such as thermal oxidation and etching.29,30

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References