Evidence for Resonant Tunneling of Electrons via Sodium Ions in Silicon Dioxide

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(Received 13 December 1984)

Metal-oxide-silicon field-effect transistors (MOSFET's) were fabricated with Na^+ ions in the gate oxide. Large peaks in the tunneling conductivity through the oxide were observed which are interpreted as resonant tunneling of electrons through localized Na^+ impurities. It was demonstrated that the tunneling current was spatially localized. The temperature dependence of several peaks was measured and found to be consistent with a simple model for resonant tunneling through localized states. The position of the state in the direction of tunneling can be determined from the temperature dependence.

PACS numbers: 71.50.+t, 73.40.Gk

The quantum mechanical tunneling current through an energy barrier containing an appropriately placed energy level can be greatly enhanced. This idea, resonant tunneling, is as old as quantum mechanics, where the problem was posed for an uncharged particle tunneling through a one-dimensional barrier from a stationary state.[1] Most experiments to test this concept have been done with charged electrons and nonstationary states. Essentially one-dimensional barriers of layered semiconductors were fabricated in 1974 by Chang, Esaki, and Tsu[2] and recently by Hirose *et al.*[3] and Sollner *et al.*[3] The tunneling current in these and related devices was enhanced at particular voltages, in good agreement with the predictions of the one-dimensional (1D) resonant-tunneling models.[4]

Less is understood about the case where the well in the barrier is not carefully prepared to be one dimensional but is simply a point defect that is finite in three dimensions. Several models have been outlined, again using the stationary-state approximation and uncharged particles.[5] Several papers[6] report a peak in the conductivity of a barrier consistent with the process of resonant tunneling through a point defect, but the difficulty in these and related experiments is verification that the peak is the result of resonant tunneling and not from some other mechanism that can produce similar peaks. To resolve this question we have prepared samples with localized states in the barrier and measured the tunneling enhancement when the states were moved and the temperature was varied. We have demonstrated that the current was passing through a local region in the barrier. We have fitted the measurements by an approximate model of resonant tunneling that includes the density of states of the incoming electrons and the three-dimensional character of the localized state. Finally, we have examined several common alternative explanations for the peaks and have done simple experiments to exclude these possibilities.

Metal-oxide-silicon field-effect-transistor (MOSFET) structures were fabricated with wet oxide gate insulators on the (100) surface of *p*-Si substrates (see inset, Fig. 1). The oxide thickness was selected to be 3.5, 4.4, or 5.1 nm. NaCl, with a nominal density of 10^{12} to 10^{13} cm^{-2}, was evaporated on the oxide immediately before the gate electrode was deposited. The Na^+ ions readily diffuse in the oxide above 300 K, and the direction of diffusion can be biased toward the SiO_2/Si interface by application of a small positive voltage (0.5 V) on the gate of the MOSFET.[7] The samples were drifted in this manner for typically 1 min at about 350 K before the cooling of the samples to 4.2

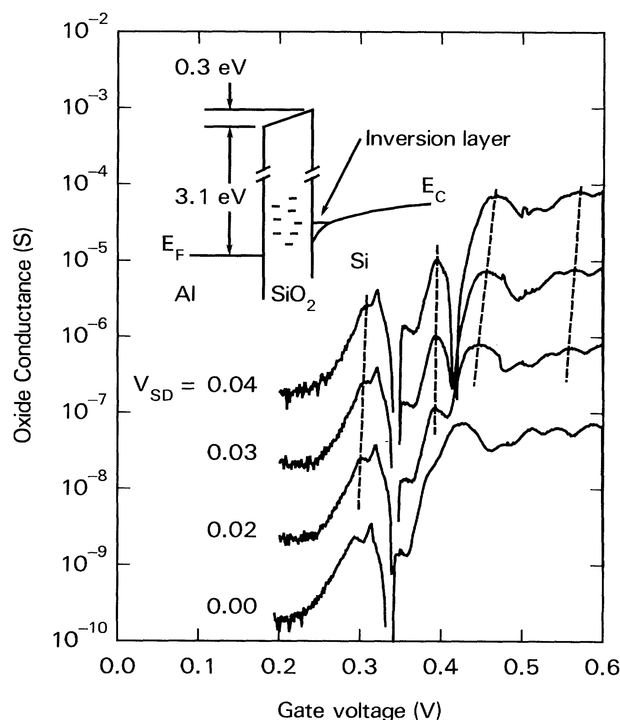

FIG. 1. Conductance vs gate voltage at 4.2 K for a typical sample for four values of the source-to-drain voltage, V_{SD}. The oxide thickness was 4.4 nm. The curves for nonzero V_{SD} are displaced for clarity. Spaces in the lines near 0.35 and 0.40 V indicate that the conductance is negative. Vertical dashed lines indicate the shift in peak positions with V_{SD}. The inset depicts the energy-band structure of the tunneling barrier. The resonant states in the barrier are symbolically depicted.

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K. While most of the Na^+ ions will remain at the Al/SiO_2 interface, a small fraction will be in the oxide. The Al gate was 15 nm thick. The channel area was 2×2 mm^2 and the source and drain contacts were formed by n^+ diffusions. The completed samples were not annealed. The source, drain, and substrate were connected together and voltage biased negatively with respect to the gate, and the tunneling conductance through the oxide was measured by means of a lock-in amplifier.

Relatively large peaks in the dynamic conductance of the current through the oxide were seen in about ten samples (Fig. 1). For a particular sample, the position and shape of each were repeatable from sweep to sweep, were independent of the direction of the voltage sweep, and remained unchanged with a steady applied voltage for many hours. Different samples had fewer or more peaks, at different voltages with different magnitudes. The dc current through the oxide at a peak was typically 10^{-11} to 10^{-8} A. The largest peaks were over 5 times larger than the local conductance background, and some had negative–dynamic-resistance regions on their high-voltage sides, e.g., near 0.35 V in Fig. 1. The threshold voltage for the samples at 4.2 K was typically 0.1 to 0.2 V, and the channel was inverted when the peaks were observed. At lower voltages the large channel impedance prevented the measurement of any current through the gate oxide. The gate-to-channel capacitance was voltage independent in the voltage range of the peaks in the conductance.

The existence of the peaks and their structure depends on Na being in the samples. In identical samples without added Na, we observed no peaks in the conductance and the current was about 10^3 times lower at similar gate voltages. Before we drifted the Na^+ ions, peaks were not seen on most of the samples. Repeated drifts at elevated temperatures with a 1-V gate bias changed the peak positions and their heights. The peak voltages after a drift were typically unrelated to the values before, and the peak voltages were not limited to a set of characteristic values, as might be expected from an inelastic-tunneling process.

A technique similar to that of Adler and Kreuzer[8] was used to demonstrate that the observed current at each peak was passing through a local site in the sample, and not distributed over the entire sample. A small dc voltage, V_{SD}, was applied between the source and drain when the channel was inverted. Then, for a given gate-to-source voltage, the net voltage from the gate to the channel was a function of position along the channel. Each peak appeared shifted when measured. The amount of shift was the difference between the gate-to-source voltage and the gate-to-channel voltage at the location where the current was passing through the oxide. In Fig. 1 different peaks shifted different amounts, which indicated different positions in the sample for each peak. Any local current path through the oxide will appear shifted. If the current had been distributed over the sample area, then the peaks would have broadened toward the high-voltage side. The sum of the voltage shifts when we measured gate-to-source and gate-to-drain voltages should have been and was equal to V_{SD}.

All peak structures measured by this technique were found to be local in origin and distributed randomly over the sample area. While this technique only measured the location of the current path along the direction from source to drain, we expect that it was spatially localized perpendicular to this direction also. We then can say that the tunneling region is localized to less than 0.1×0.1 mm. The actual size of the tunneling regions was most likely smaller, and of a length scale related to the Na^+ ions. The increasing conductivity at high gate voltages was spatially localized since it shifted in a complicated way with V_{SD}. In some samples this conductivity was a sum of many overlapping peaks (Fig. 1). In other samples it appeared not to be, but rather an exponential rise in conductance with voltage.

The temperature dependence of several peak structures was measured and two examples are shown in Figs. 2 and 3. The full width at half maximum of each peak increased with increasing temperature but not linearly or in any other simple way. The maximum conductivity of each peak above the background decreased with increasing temperature, again, not in any simple way. The upper section of Fig. 3 plots the voltage at the peak in the conductivity as a function of

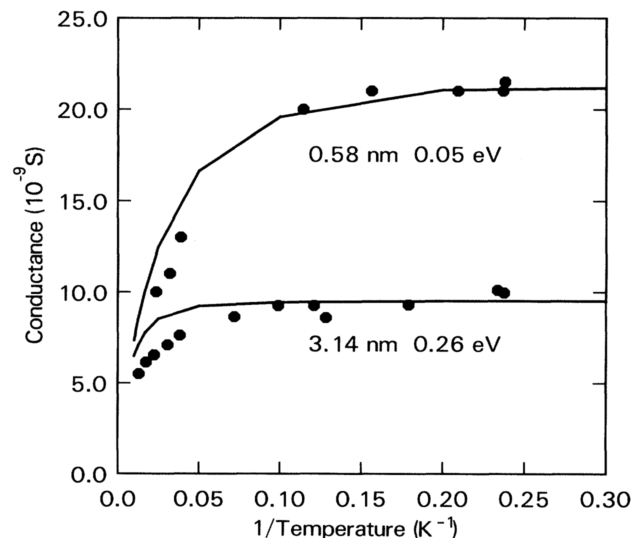

FIG. 2. Measured conductance at peak vs inverse temperature for two samples (dots). The oxide thickness was 3.6 nm. Predictions of model for a resonant state located at a stated distance from the SiO_2/Si interface and stated energy above the unbiased Fermi energy (lines).

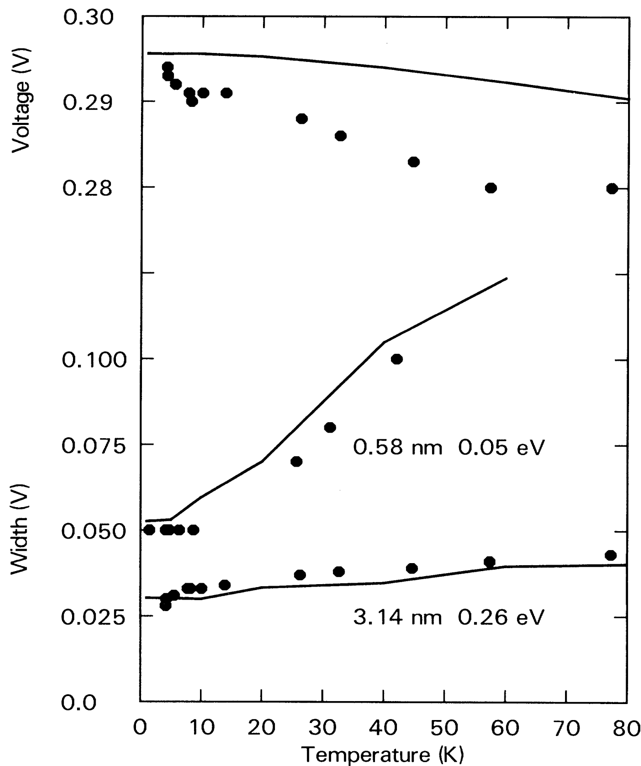

FIG. 3. Measured full width at half maximum at peak vs temperature for the same two samples as Fig. 2 (dots). Predictions of model (lines). Upper curve: measured voltage at peak vs temperature for narrower peak (dots). Predictions of model for position (line).

temperature of the narrower peak.

We believe that the measured data are consistent with resonant tunneling of electrons through Na-related states in the oxide. The positive electrostatic charge of the Na^+ ions will reduce the average energy barrier that a tunneling electron experiences[9] and should have increased the direct tunneling current. The magnitude of the observed conductivity significantly exceeds what is expected for a barrier of the nominal width and height (3.1 eV). The barrier is not uniformly reduced, but spatially modulated by the pointlike charges of the Na^+ ions, which thus create many localized states of varying energies. A state with an energy level less than about 0.1 or 0.2 eV away from the Fermi energy would explain the voltage scale of a typical measured peak. There is little known about the energy levels of Na in bulk SiO_2, but there are no known energy levels within 0.1 or 0.2 eV of the equilibrium Fermi energy.[9] The Na does introduce a large number of interface states near the Fermi energy.[10] The observed peak structure cannot be an average result of many independent Na atoms since a single drift would not change all these atoms in the same identical way. The electron current passing through the oxide at the peak position, 10^8 to 10^9 electrons/sec, is not too large to be passing through a single atomic-size region.

Of the estimated 10^{10} Na atoms in the sample, even if an extremely small fraction are in the oxide and active, many more are potentially in the barrier and at a particular energy level than the number of peaks seen on an individual sample (1 to 10). A single typical Na atom cannot account for a single peak. If the fraction of contributing atoms is exponentially small or a function of special enviornmental conditions, we could understand the relatively few peaks measured per sample. We believe that the peaks probably resulted from a relatively rare arrangement of one or more Na atoms, e.g., an unlikely chemical state, clustering of Na atoms,[11] an unusual positional configuration of a single atom or atoms, or the proximity of some other defect or impurity to a Na atom. The spatial localization of the tunneling region also suggests that the conditions are rare.

Resonant enhancement of the tunneling current through a one-dimensional barrier has been investigated theoretically by many authors.[4] The 1D theory is not expected to apply rigorously to our case where the resonant states in the barrier are point defects and the incoming electrons are not in plane-wave states but in the two-dimensional inversion layer of the MOSFET. For the lack of a complete 3D theory we made use of an approximate expression for the tunneling current:

$$J(V) \propto \int_0^\infty N(E)D(E)\,dE. \qquad (1)$$

We have taken $D(E)$ to be the 1D stationary-state tunneling probability[4] for an electron having an energy E, and $N(E)$ is the number of electrons that can tunnel at an energy D:

$$N(E) \propto N_{\mathrm{Si}}(E)N_{\mathrm{Al}}(E+eV) \times [f(E)-f(E+eV)], \qquad (2)$$

where N_{Al} and N_{Si} are the usual densities of states in the Al and in the Si inversion layer, and $f(E)$ is the Fermi function. This is an approximate model, yet it includes two relevant characteristics of tunneling through a point defect in a MOSFET. Since the tunneling is through a point defect, the electron momentum perpendicular to the tunneling direction can change, so that the total electron momentum or energy is used to calculate $D(E)$, not just the momentum or energy in the tunneling direction. The predicted tunneling current is very dependent on the density of electron states in the inversion layer, so that this must be accurately included in the model.

The predictions (Figs. 2 and 3, solid lines) are in good agreement with the measured data. As the gate voltage is inceased the energy of each resonant state decreases relative to the Fermi energy of the inversion layer. The peak in conductivity occurs when the

resonant-state energy passes through the Fermi energy and the tunneling current increases rapidly. The negative dynamic conductance occurs when the resonant-state energy goes below the bottom of the Si conduction band and the resonant-tunneling curent decreases. The negative conductance may not be observed if the individual peaks are too close in energy or the total measured current is increasing rapidly from tunneling in other places on the oxide. The peak in conductivity through each resonant state has a finite width in voltage at $T=0$ which is inversely related to the tunneling time out of the resonant state. When the position of the resonant state is moved so as to increase the tunneling current through the state, the width in voltage at $T=0$ decreases. The model also predicts a small shift in peak voltage with temperature, and this is plotted in Fig. 3 for one localized state.

As the temperature is increased additional width is observed because $N(E)$ broadens, and this was used to locate approximately the position of the localized state in the direction of tunneling. A small change in gate voltage will translate to a reduced change in energy level, with respect to the Fermi energy of the inversion layer, of a localized state depending upon its position, i.e., $\Delta E = \alpha \Delta V_G$, where α is the fraction of the distance the localized state is across the oxide barrier. The temperature broadening of the incoming electron distribution will broaden the measured width with respect to the gate voltage by $kT_B/\alpha e$. In Figs. 2 and 3, the lower curve represents a localized state very near the Al gate, since the temperature broadening was very close to kT_B/e, i.e., α was close to 1. On the the other hand, the additional broadening of the state in the upper curve was about 6 times kT_B/e and hence α was about $\frac{1}{6}$. The state was about 0.6 nm away from the SiO_2/Si interface. As the temperature was lowered a temperature-independent width and height was reached that can be related to the quantum mechanical lifetime of the state.

We believe that the primary conduction mechanism through the oxide was not inelastic tunneling through a local region in the oxide, nor conduction through a filament or microshort in the oxide.[12] Inelastic tunneling can create peaks in the second derivative of the current, but usually not in the first derivative, i.e., the conductance. The voltage at the maximum of each peak in an inelastic tunneling process would have been characteristic of the inelastic process and not almost arbitrary. Also, the increase at the peak would have been much less than the local background. Neither was observed. Since the electrons tunneled from the inversion layer to the Al gate, and only the lowest inversion layer subband was filled, the measured peaks were not caused by the subband structure in the Si inversion layer.[13] Several samples, after exposure to reltively high voltages, had 10^3 to 10^5 times the conductivity of the sample in Fig. 1 and an increase in conductivity from 0.0 to 0.6 V of about 10 times. These samples, when viewed with an optical microscope, showed evidence of craterlike breakdown in the Al gate and oxide. The samples reported here displayed no such evidence. However, the special conditions necessary for a Na atom to produce resonant tunneling may be similar to those necessary for a filamentary breakdown of the oxide.[14] Trapping of electrons in the oxide has also been shown to produce similar structure on the tunneling characteristics.[15] Electron trapping should have produced characteristics that change with time and oxide capacitances that increase abruptly at the voltage of each peak, neither of which occurred.

In conclusion, we have shown evidence for resonant tunneling through point defects in a tunnel barrier. The presence of the resulting peaks in conductivity at specific voltages depended on the presence of Na^+ ions in the oxide and the positions of the ions determined the peak voltages. The tunneling region was spatially localized. The temperature dependence of the peak heights and widths was approximately fitted by a simplified model of resonant tunneling through point defects.

The authors thank D. J. DiMaria, M. Ya. Azbel, T. W. Hickmott, and F. Stern for stimulating conversations and J. A. Tornello for technical assistance.

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