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Bipolar conductivity in amorphous HfO_2

D. R. Islamov,[1,a)] V. A. Gritsenko,[1,b)] C. H. Cheng,[2] and A. Chin[2]
[1]*A. V. Rzhanov Institute of Semiconductor Physics, Siberian Branch of Russian Academy of Sciences, Novosibirsk 630090, Russia*
[2]*National Chiao Tung University, Hsinchu 300, Taiwan*

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This study calculates the contribution of electrons and holes to HfO_2 conductivity in Si/HfO_2/Ni structures using experiments on injection of minority carriers from *n*- and *p*-type silicon. Results show that electrons and holes contribute to the conductivity of HfO_2, allowing HfO_2 to exhibit two-band conductivity. © *2011 American Institute of Physics*. [doi:10.1063/1.3626599]

Knowledge about charge transport mechanisms in dielectrics is crucial to ensuring the reliability of silicon devices. The charge sign of carriers in semiconductors can be found by measuring Hall effect and thermoelectric power. However, these methods are not applicable to dielectrics due to the very low density of mobile charge carriers. The charge sign of the carriers in dielectrics can be found using experiments on the injection of minority carriers from *n*- and *p*-type silicon[1,2] in metal-insulator-semiconductor (MIS) structures or separating the electrons and holes of the total current in a metal-oxide-semiconductor field-effect transistor (MOSFET).[3]

The conductivity of dielectrics can be monopolar or bipolar. For example, the conductivity of MIS with thermal SiO_2 (Ref. 4) and the conductivity of Al_2O_3 (Ref. 5) are monopolar, namely, electronic. At the same time, Si_3N_4 (Refs. 1 and 3) and ZrO_2 (Ref. 6) have bipolar conductivity.

Scientific literature presents contradictory findings regarding the charge sign of carriers in HfO_2. Some authors[7–10] considered the presence of electronic traps in HfO_2. Others[9,10] investigated the conductivity mechanism in HfO_2 and found that the energy range of the traps is 1.36–1.5 eV. However, experimental findings must confirm the energy range electron traps. Therefore, this study determines the carriers charge sign in HfO_2 using experimental measurements on the injection of minority carriers from *n*- and *p*-type silicon.

Samples were cleaved from the wafers of Si with HfO_2 film with a thickness of 150 Å. The HfO_2 films were deposited by physical vapor deposition (PVD) on *p*- and *n*-type Si substrates. Low post-deposition annealing (PDA) at 350°C was applied to prevent the growth of interfacial SiO_x.[11] Structural analysis shows that the resulting HfO_2 films were amorphous. The samples for transport measurements were equipped with Ni gates of square form 1.1×1.1 mm^2 for electrical contact. Current-voltage (*I*-*V*) and capacitance-voltage (*C*-*V*) measurements were taken at room temperature. *C*-*V* measurements were taken at a frequency of 100 kHz. A tungsten lamp was used for light illumination, and the substrate was *n*- and *p*-type silicon.

Figure 1(a) shows the *I*-*V* curves of the *p*-Si/HfO_2/Ni MIS structure for depletion and accumulation modes in the dark (thick line) and under illumination (thin line). In accumulation mode, when a negative potential is applied to the Ni contact, almost all the applied voltage drops across the dielectric and the current increases exponentially with increasing electric field. When a positive potential is applied to metal contact, i.e., in the depletion mode, the current increases exponentially at low voltages. Current saturation appears at a sufficiently large voltage. The saturation level increases under illumination. The saturation current and its increase under illumination indicate that in the depletion mode minority carriers are injected from Si into HfO_2. The minority carriers are electrons in this case. Independent

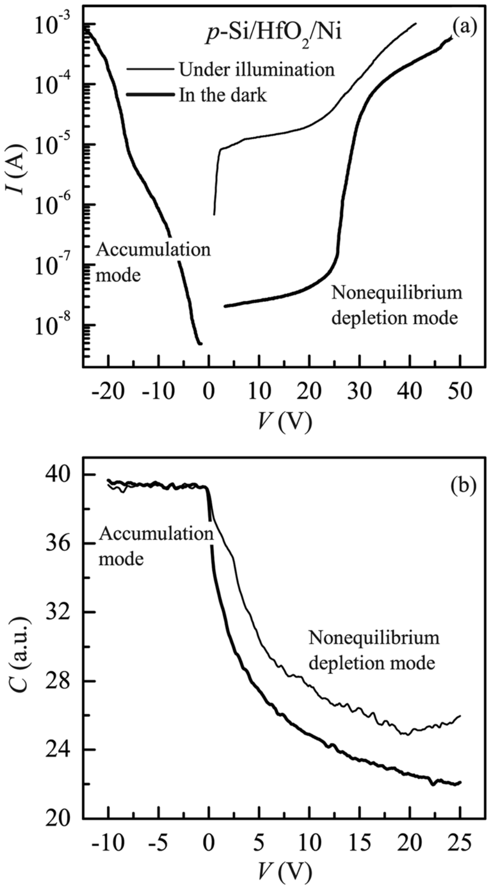

FIG. 1. (a) *I*-*V* curves for *p*-Si/HfO_2/Ni MIS structure for depletion and accumulation modes in the dark (thick line) and under illumination (thin line). (b) *C*-*V* curves for the same structure and conditions.

[a)] Electronic mail: damir@isp.nsc.ru.
[b)] Electronic mail: grits@isp.nsc.ru.

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confirmations of the minority carriers injections include: (1) the existence of capacity transition from inversion mode to nonequilibrium depletion mode and (2) capacity increasing in nonequilibrium depletion mode under illumination (Fig. 1(b)).

Figure 2(a) shows the energy band diagram of the *p*-Si/HfO_2/Ni structure based on photoemission data and photoconductivity measurements.[12] The energy barrier for electrons on Si/HfO_2 surface is 2.0 eV, and the barrier for holes is 2.5 eV. The band gap in HfO_2 is 5.6 eV. The energy barrier for electrons on Ni/HfO_2 surface is 2.5 eV. When a positive potential is applied to the Ni, electrons from the inversion layer are injected into silicon (Fig. 2(b)). Increasing the positive charge on Ni is not screened by the charge of electrons in the inversion layer but the charge of negatively charged acceptors in the depletion layer. For this reason, the increment of total voltage is not screened by the incremented potential in the dielectric when increasing of the voltage drop on the depletion layer. Illumination causes an additional photogeneration of minority carriers (electrons) (a twisted arrow in Fig. 2(b)), which subsequently increases the dielectric current. Thus, when a positive potential is applied to the Ni contact, the conductivity of HfO_2 is carried, at least in part, by electrons injected from the silicon. If the conductivity of positive potential applied to the Ni was carried by holes injected from the Ni, then the effects of nonequilibrium depletion in silicon is not be apparent.

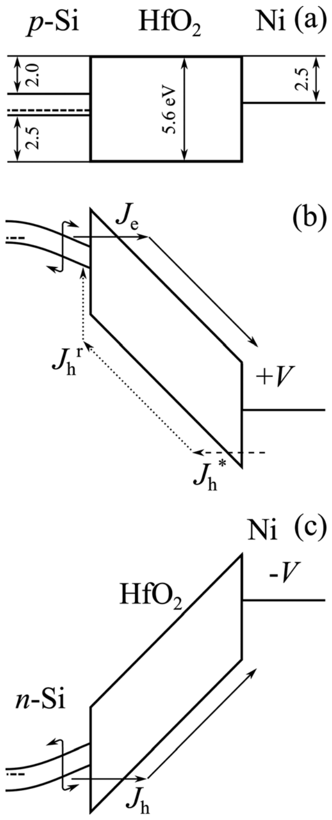

FIG. 2. (a) The energy band diagram of *p*-Si/HfO_2/Ni structure in flat band mode. (b) The same diagram with the positive bias $+V$ applied to the Ni contact. J_h^* is a flow of injected from the metal into HfO_2 holes, J_h^r is a recombination flow of injected from HfO_2 into Si holes, and J_e is a flow of injected from Si into HfO_2 electrons. (c) The energy band diagram of *n*-Si/HfO_2/Ni structure with the negative bias $-V$ applied to the Ni contact. J_h is a current of injected from Si into HfO_2 holes.

The description above raises a question about the possibility of recombining holes injected from the insulator with electrons in surface states and with electrons from the inversion layer in Si. Holes injected from the insulator into the silicon can generally recombine with electrons in the surface states on the Si/HfO_2 interface. Figure 2(b) illustrates this process, which simulates the injection of electrons from the silicon into the insulator. This study estimates the probability of recombining holes and electrons in the surface states on the Si/HfO_2 interface. A typical recombination cross-section of electrons in the surface states on the silicon-insulator interface is $\sigma \sim 10^{-16}$ cm^2. Thus, if the concentration of the surface states is $N_s \sim 10^{11}$ cm^{-2}, the probability of recombination will be $W = \sigma N_s \sim 10^{-5} \ll 1$. This estimation indicates a negligible contribution to the recombination of injected from the insulator holes with electrons in the surface states. The probability of recombination of injected from the insulator holes with electrons in the inversion layer is low since the thickness of the inversion layer is less than the diffusion length of the holes.

Figures 3(a) and 3(b) show *I*-*V* and *C*-*V* dependencies for *n*-Si/HfO_2/Ni structures, respectively. With a positive voltage bias on the Ni contact, i.e., in accumulation mode, the current grows with increasing of voltage exponentially. Current saturation appears in depletion mode, and the saturation level increases under illumination. This phenomenon

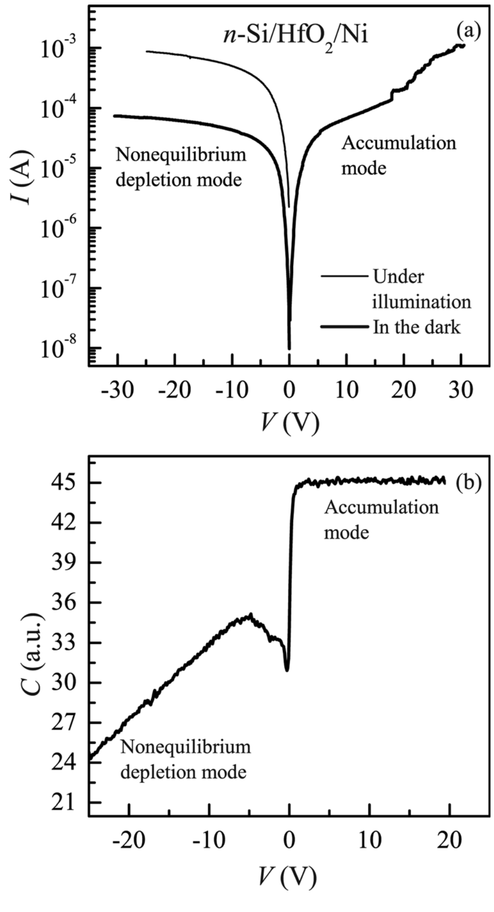

FIG. 3. (a) *I*-*V* curves for *n*-Si/HfO_2/Ni MIS structure for depletion and accumulation modes in the dark (thick line) and under illumination (thin line). (b) *C*-*V* curve for the same structure in the dark.

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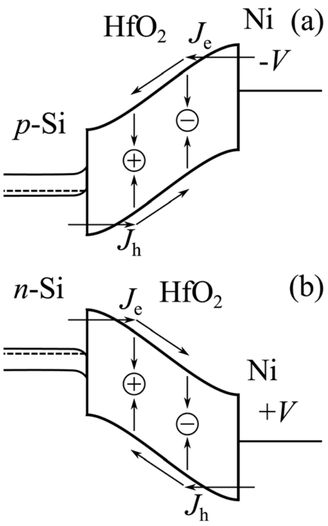

FIG. 4. (a) The energy band diagram of p-Si/HfO$_2$/Ni MIS structure with the negative bias $-V$ applied to the Ni contact. (b) The same diagram of n-Si/HfO$_2$/Ni MIS structure with the positive bias $+V$ applied to the Ni contact.

also takes place in depletion mode in p-Si/HfO$_2$/Ni structures.

The presence of the current saturation in depletion mode in n-Si/HfO$_2$/Ni structures reveals the injection of minority carriers (holes) from silicon substrate into hafnium oxide (Fig. 2(c)). The capacity transition to nonequilibrium depletion mode shown in Fig. 3(b) confirms this statement. The probability of recombination of injected from the insulator electrons with holes in the inversion layer is negligible, as in a p-Si substrate.

In conclusion, this study presents experiments on separating the carrier signs in HfO$_2$ using n- and p-Si in depletion mode. Results demonstrate that the conductivity in HfO$_2$ is bipolar (or two-band), much like the conductivity in Si$_3$N$_4$ and ZrO$_2$. This conclusion agrees with the experiments on the separation of currents in a transistor.[13] The electrons were injected from a negatively biased contact, while the holes were injected from a positively biased contact (Fig. 4). As in Si$_3$N$_4$, the free electrons recombined with holes trapped at hole traps, and the free holes recombined with electrons localized on the electron traps in bulk insulator.

Previous studies determined the trap energy of HfO$_2$ (Refs. 9 and 10) based on the hypothesis that the type of the traps is electronic. Since this study shows that the conductivity in HfO$_2$ is bipolar, indeterminacy arises if the parameters belong to an electron or hole trap. This study assumes that the energy levels of electron and hole traps in HfO$_2$ and in Si$_3$N$_4$ are equal.[14] However, the proof of this statement requires further investigation.

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