Bipolar conductivity in nanocrystallized TiO2

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Bipolar conductivity in nanocrystallized TiO_2

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This study calculated the contribution of electrons and holes to TiO_2 conductivity in Si/TiO_2/Ni structures by conducting experiments on the injection of minority carriers from *n*- and *p*-type silicon. Results show that electrons and holes contribute to the conductivity of TiO_2, enabling two-band conductivity. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737016]

Universal memory in electronic devices must have the best properties of modern memory types. It must be as fast as random access memory (RAM), have an unlimited number of write cycles, and must be non-volatile, as in hard drives and flash and solid-state drive (SSD). A recently discovered resistive memory effect in high-κ dielectric films provides the opportunity to create such types of universal memory for electronic devices.[1] Because this resistive memory effect was discovered in films of TiO_2,[2] this material may be used in the production of new memory chips in the future.

To obtain silicon devices with most optimal properties, it is crucial to comprehend charge transport mechanisms in dielectrics. The conductivity of dielectrics can be monopolar or bipolar. In other words, the charge carriers can be electrons or holes only, or electrons and holes simultaneously, i.e., the conductivity can be one-band or two-band. For example, the conductivity of metal-insulator-semiconductor (MIS) with thermal SiO_2 (Ref. 3) and the conductivity of Al_2O_3 (Ref. 4) are monopolar (electronic), whereas Si_3N_4 (Refs. 5 and 6) and ZrO_2 (Ref. 7) have bipolar conductivity.

Scientific literature presents theoretical models of charge transport mechanisms in titanium dioxide films, describing a resistive memory effect while considering only electrons as charge carriers.[8,9] The authors[8,9] considered the presence of electronic traps in reduced Ti ion centers or oxygen vacancies because of the weak Coulombic interaction. No researcher has yet attempted to evaluate the contribution of holes in the charge transport, neither theoretically nor experimentally. Therefore, this study determines the carriers charge sign in TiO_2 using experimental measurements of the injection of minority carriers from *n*- and *p*-type silicon in MIS structures.[5,10]

Samples were cleaved from Si wafers with TiO_2 film, with a thickness of 150 Å. The TiO_2 films were deposited by physical vapor deposition (PVD) on *p*- and *n*-type Si substrates. Low post-deposition annealing (PDA) at 300 °C was applied to prevent the growth of interfacial SiO_x. Structural analysis shows that the resulting TiO_2 films underwent nanocrystallization.[11] The TiO_2 capacitors fabricated at higher temperatures showed a poly-crystalline structure by x-ray diffraction (XRD) spectra and a very large leakage current via grain boundary conduction.[12] The leakage current is greatly reduced by 6 orders of magnitude in a nanocrystallized TiO_2 material without grain boundary conduction.[11] The samples for transport measurements were equipped with Ni gates of a square form of 1.1×1.1 mm^2 for electrical contact. The Si substrate was used as the ground contact. Current-voltage (*I-V*) measurements were taken at room temperature. A tungsten lamp was used for illumination.

Fig. 1 shows the energy band diagram of *n*-Si/TiO_2/Ni (a), (c), (e) and *p*-Si/TiO_2/Ni (b), (d), (f) structures in flat band mode (a), (b) and with applied bias voltage (c)–(f).

When a positive potential is applied to Ni contact for *n*-Si/TiO_2/Ni (Fig. 1(c)), the electronic system is in accumulation mode, and conductivity is provided by major carriers

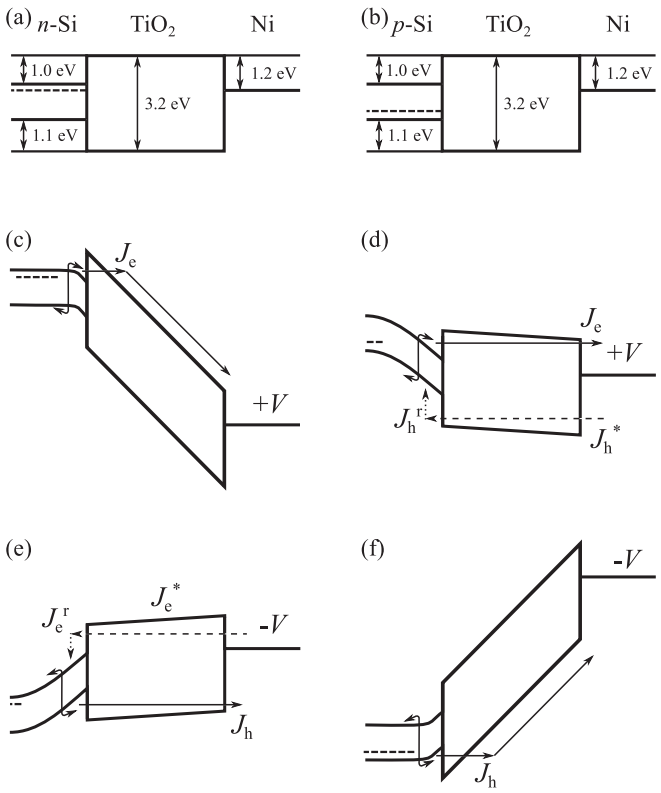

FIG. 1. Energy band diagram of *n*-Si/TiO_2/Ni (a) and *p*-Si/TiO_2/Ni (b) structures in flat band mode. The same diagrams in accumulation (c), (f) and depletion mode (d), (e). J_e/J_h are flows of injected electrons/holes from Si into TiO_2, J_e^*/J_h^* are flows of injected electrons/holes from the metal into TiO_2, J_e^r/J_h^r are recombination flows of injected electrons/holes from TiO_2 into Si.

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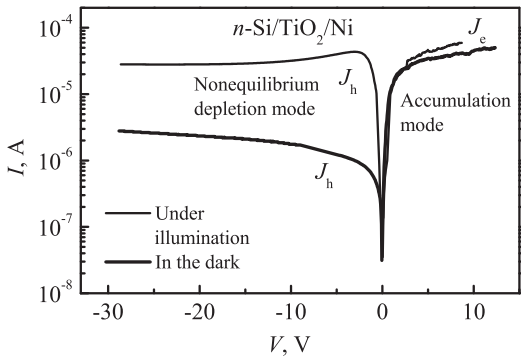

FIG. 2. Experimental *I-V* curves for *n*-Si/TiO_2/Ni MIS structure for depletion and accumulation modes in the dark (thick line) and under illumination (thin line). TiO_2 film thickness is 150 Å.

(electrons). The current through the TiO_2 dielectric films J_e is relatively high. When a negative potential is applied to the Ni contact, the system falls into non-equilibrium depletion mode, and the current in dielectric is a flow of injected electrons from the metal into TiO_2 J_e^*. Fig. 2 shows the experimental *I-V* curves of the *n*-Si/TiO_2/Ni MIS structure. The *I-V* plate illustrates that J_e^* (thick line, $V<0$) is substantially less than J_e (thick line, $V>0$). Illumination causes an additional photogeneration of minority carriers (holes) (a twisted arrow in Fig. 1(e)), which subsequently increases the dielectric current J_h. This dramatic growth of the dielectric current is shown in *I-V* plate by the thin line in Fig. 2. The current increases exponentially at low voltages, and current saturation appears at a sufficiently large voltage. The current saturation level increases under illumination, and this rise indicates that the depletion mode minority carriers (holes, in this case) are injected from Si into TiO_2.

Fig. 3 shows *I-V* dependencies for *p*-Si/TiO_2/Ni structures. With a negative potential applied to Ni for *p*-Si/TiO_2/Ni (Fig. 1(f)), i.e., when in accumulation mode, the current grows exponentially with increasing voltage. Current saturation appears in depletion mode, and the saturation level increases under illumination. This phenomenon also occurs in depletion mode in *n*-Si/TiO_2/Ni structures. The current saturation level in *p*-Si/TiO_2/Ni structures indicates the injection of minority carriers (electrons) from the silicon substrate into titanium dioxide.

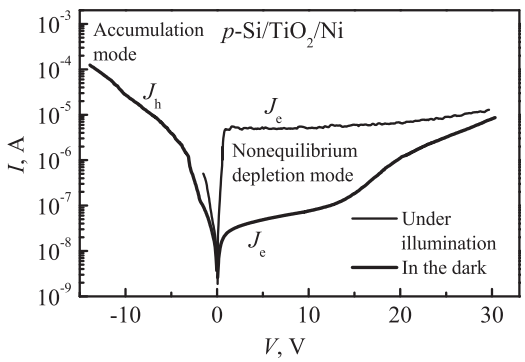

FIG. 3. Experimental *I-V* curves for *p*-Si/TiO_2/Ni MIS structure for depletion and accumulation modes in the dark (thick line) and under illumination (thin line). TiO_2 film thickness is 150 Å.

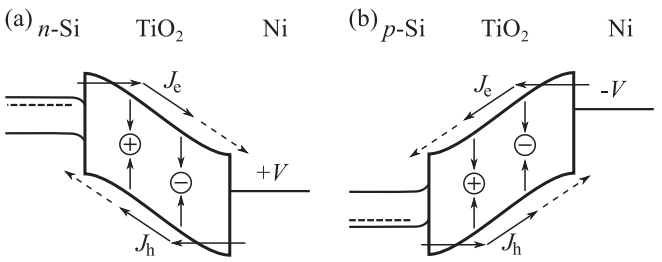

FIG. 4. (a) Flows of charge carriers in *n*-Si/TiO_2/Ni MIS structure with the positive bias $+V$ applied to the Ni contact (a). (b) The same diagram of *p*-Si/TiO_2/Ni MIS structure with the negative bias $-V$ applied to the Ni contact. Dashed arrows show the flows of not recombined charge carriers.

In conclusion, this study presents experiments on separating carrier signs in TiO_2 using *n*- and *p*-Si in non-equilibrium depletion mode. Results demonstrate that TiO_2 conductivity is two-band, similar to that in Si_3N_4,[5,6] ZrO_2,[7] and HfO_2.[13]

As in Si_3N_4, and HfO_2, the delocalized free electrons recombined with holes trapped at hole traps, and the free holes recombined with electrons localized on the electron traps in the bulk insulator (Fig. 4). The probability of recombining holes and electrons in the surface states on the Si/TiO_2 interface is negligible, similar to that which occurs in HfO_2,[13] which also indicates that the major carriers current from the metal gate $J_{e,h}^*$ is much less than the current of minority carriers $J_{h,e}$ under illumination. 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. The flows of not recombined charge carriers are shown in the Fig. 4 by dashed arrows.

The new results must be considered in further investigations for the creation of more accurate models of transport mechanisms in titanium dioxide films to describe different effects, including the resistive memory effect.

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