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Article

The negative differential resistance of nitrogen implanted TiO_2

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Abstract: The microstructure and negative differential resistance (NDR) effect of nitrogen implanted rutile TiO_2 were investigated by measuring the XPS, Raman spectra and current voltage curves. It was found that the light illumination has large influence on the NDR effect. Under the illumination of 60 mW laser light, a large NDR with a small electric field (1250 V/cm) is obtained. This electric field is about three orders smaller than that reported in literature (1×10^6 V/cm). The electric field induced tunneling is the possible mechanism of electric transport at higher field region. The NDR is thought to be related to the light and nitrogen dopant induced reaction including the destroying of water, the scavenging of electron, and the surface oxidation transform of non-stoichiometric TiO_{2-x} to stoichiometric insulating state. The results of this paper are not only useful in understanding the mechanism of NDR, but also useful in providing an effective method in manipulation NDR.

Keywords: negative differential resistance; nitrogen implanted TiO_2; light assistance

1. Introduction

More and more attention has been paid to nitrogen doped TiO_2 due to its interesting property and various potential applications including photo catalyst [1–3], diluted magnetic semiconductor [4–6], thermo-electronics [7], electron field emission [8] and electrical transport property [9,10]. It is found that oxygen vacancy can be favorably generated in nitrogen doped TiO_2 since the formation energy of oxygen vacancy in TiO_2 is largely decreased by nitrogen doping [1]. TiO_2 is changed from insulator to semiconductor since the electrical resistivity of TiO_2 was reduced by the formation of oxygen defects [7]. The band gap of TiO_2 can be effectively decreased. The photo catalyst activity under visible light can be greatly enhanced [1–3]. Magneli phase of Ti_n $(O, N)_{2n-1}$ can also be obtained [7]. Furthermore, it was found that the oxygen vacancy of nitrogen doped TiO_2 has better stability than that of pure TiO_2 [8].

It is well known that the generation and redistribution of oxygen vacancies are closely related to many interesting phenomena such as the NDR and the resistance switching (RS) of TiO_2 [11–15]. For example, the generated oxygen vacancies can migrate under bias voltage and then form conductive filaments [14]. Once two metal electrodes are connected by conductive filaments, materials are changed from high resistance state to low resistance state because current can pass through these filaments. On the other hand, due to the Joule heat or the ionic migration, filaments rupture and materials are changed into high resistance state. However, there are few reports on NDR and RS of nitrogen doped TiO_2.

The NDR and RS effect of TiO_2 have been studied intentionally as there are a lot of potential applications such as the resonant tunneling transistors, oscillators, multipliers, and resistive random-access memory [11–16]. NDR and RS of TiO_2 were thought to be related to the oxygen vacancies, phase changing and electrical

chemical reaction. For example, Kim et al. [11] indicated that NDR is the result of local surface oxidation under bias voltage. The electrical current maximum state is obtained as the oxygen vacancies are formed and subsequently ordered and ultimately leaded phase change from a nonconductive fully-oxidized phase to a conductive oxygen-deficient Magnéli phase [11]. The electrical current minimum state is obtained when the non-stoichiometric TiO_2 transforms to the stoichiometric insulating state. Zhao et al. [13] assigned the NDR to the damage of hydrogen-bonds among water molecules to break the continuous water layer. Wang et al. [12] assigned the NDR of $Pt/BiFeO_3/TiO_2/BiFeO_3/Pt$ to the polarization field in the two $BiFeO_3$ layers which causing the movement of electrons to be bound. Kamaladasa et al [16] found that the bias voltage induced reversible bipolar RS in TiO_2 is companied with the reversible formation and dissociation of shear faults. The shear faults are induced by the increasing of oxygen vacancy concentration to some extent [16].

2. Experiments

Experimentally, the single crystal TiO_2 substrates were available from Hefei Kejing Materials Technology Co.Ltd. The nitrogen implantation was performed at the energy of 60 keV in a vacuum chamber of 2×10^{-3} Pa, with the nominal dose of 1×10^{18} ions cm^{-2}. The substrate was kept at room temperature by the circulation of cooling water during ion implantation. The samples' stoichiometry was measured by a KRATOS X SAM 800 x-ray photoelectron spectroscopy (XPS). Raman spectra were obtained by a HORIBA LABRAM HR laser Raman spectrometer. The current voltage curve was measured using two terminal methods. The distance between the two electrodes is about 2 mm. The sample size for I-V measurement is about $4 \times 5 \times 0.5$ mm^3. The light illumination is using a laser with the wavelength of 405 nm. The laser beam diameter is about 2.5 mm.

3. Results and discussions

In a previous paper [4], the microstructure, light absorption, magnetism and electrical transport property of nitrogen implanted TiO_2 single crystal were investigated. It was found that the nitrogen implanted TiO_2 is with a single rutile crystal structure. The absorption in the visible light region is greatly enhanced with nitrogen implantation. Room-temperature ferromagnetism is obtained in the sample with an implanted dose of about 1×10^{18} ions/cm^2. The sample changes from insulating to semiconductor when nitrogen doping increasing to 1×10^{18} ions/cm^2. The incorporation of nitrogen is confirmed by XPS measurements.

Figure 1 shows the full-survey and high resolution XPS of the sample with an implantation dose of about 1×10^{18} ions/cm^2. Obviously seen in the full-survey spectrum, only four elements, Ti, N, O, and C, are found in this sample. The signal from carbon is mainly introduced by the surface contamination during the XPS measurement. There are no other elements being detected by XPS. The high-resolution N1s spectrum has a broad spectrum ranged from 395eV to 404eV, with the maximum located at about 401 eV. This behavior is similar as that reported in literature [3,17]. The high-resolution N1s spectrum can be fitted by two peaks

located at 399.4 and 402.0 eV, respectively. The peak near 399.4 eV was ascribed to interstitial nitrogen doping with structure of Ti–O–N [10]. The peak near 402 eV was ascribed to titanium oxynitrides [9]or to substantial nitrogen doping with structure of O–Ti–N [3]. It should be kept in mind that the nitrogen state in the doped TiO_2 varies from case to case. For example, peaks at 396–397 eV were attributed to substitutional nitrogen [9]. Peaks at higher binding energies (~400 eV) were ascribed to a generic interstitial site [1]. In the other hand, the signal at 401.3 eV was attributed substitutional nitrogen [3]. The high resolution Ti $2p_{3/2}$ spectrum can be fitted by two peaks located at 458.2 and 458.8 eV. The peak at 458.8 eV was ascribed to stoichiometry TiO_2 crystals. The peak at 458.2 eV was assigned to nitrogen doped TiO_2 structure [8]. There is a 0.6 eV shift to lower binding energy for nitrogen doped TiO_2, which indicates the increasing in electron density around Ti atoms in the nitrogen-doped TiO_2 [8]. The formation of oxygen vacancies induced by nitrogen doping was thought to be responsible for the electron density increasing by reducing the valence state of Ti^{4+} to lower states Ti^{3+} [8]. The high resolution O1s spectrum can be fitted by two peaks located at about 530.8 and 529.9 eV, respectively. The peak near 530.8 eV was assigned to TiO_2. The peak near 529.9 eV was ascribed to nitrogen doped TiO_2 structure [3].

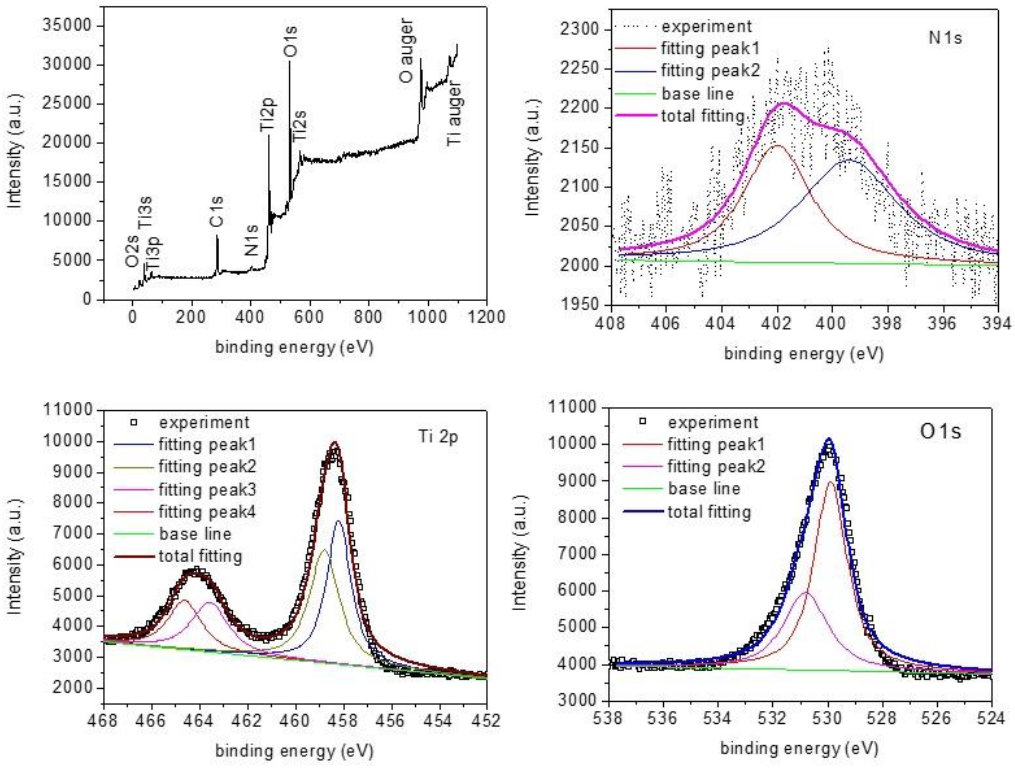


Figure 1. The full-survey and high resolution XPS of the nitrogen implanted TiO_2 sample.

Figure 2 shows the Raman spectra of nitrogen implanted TiO_2 sample. There are peaks located at about 141, 237, 445, and 611 cm^{-1} in the Raman spectra, which can be assigned to the B_{1g} (141 cm^{-1}), two phonon processes E_g(237, 448 cm^{-1}), and A_{1g} (611 cm^{-1}) Raman active modes of the rutile phase TiO_2 [10]. There are no fundamental Raman active modes from anatase phase titanium dioxide including A_{1g} (519 cm^{-1}), B_{1g} (399 cm^{-1}) and E_g (197 and 639 cm^{-1}) [18], indicating that the

sample is of pure rutile structure.

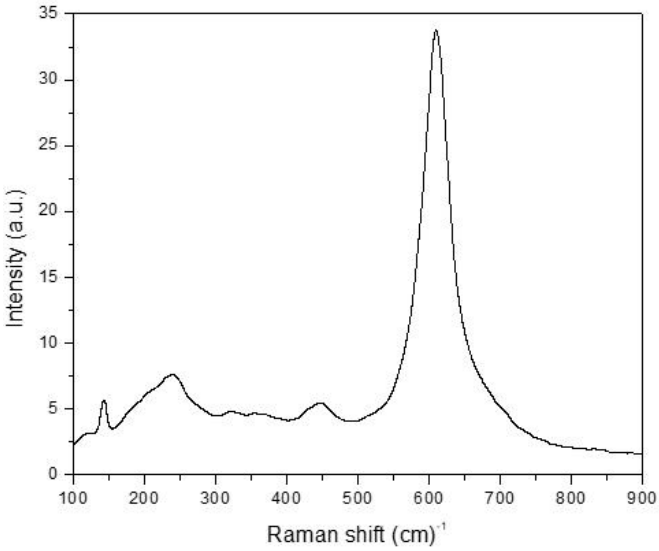
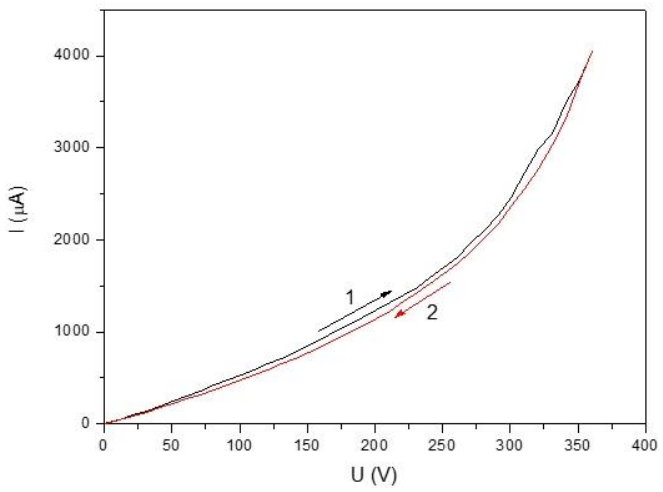
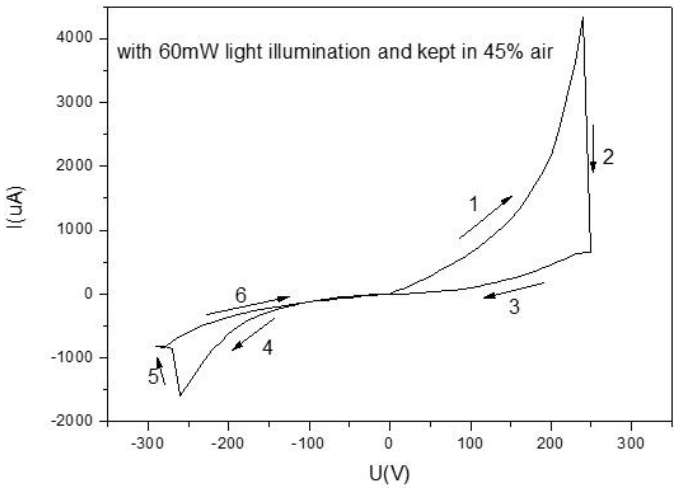


Figure 2. Raman spectra of nitrogen implanted TiO_2 sample.

The current–voltage (I-V) curve of nitrogen implanted TiO_2 sample is shown in **Figure 3a,b**. As seen in **Figure 3a,** without light illumination, there is no NDR in the bias voltage region from 0 to 350 V. The current increases no linearly with voltage increasing. There is little hysteresis between the I-V curves measured with voltage varying from 0 to 350 and then back to 0 V. This behavior indicates that there are little RS effect and NDR without light assistance. The reason should be due to that the bias voltage is not large enough [14]. When the bias voltage is small, it may only generate electronic current and little influence on the chemical or physical state of the materials, and in this situation, the I-V curves are non-hysteretic and closed. When the bias voltage is high enough, the ionic movements and/or the redox reactions are likely to initiate to alter the chemical or physical state of the materials, and in this case, the I-V curves are expected to become hysteretic and open [14]. Since NDR in TiO_2 usually appears with an electric field of about 1×10^6 V/cm [19], the bias voltage should be about 2×10^5 V to induce NDR for our sample.



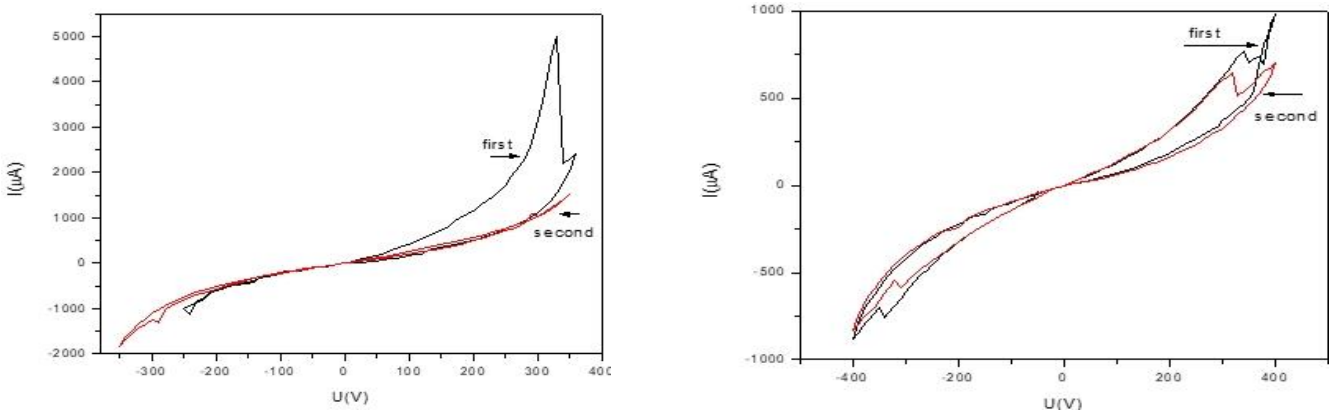
(a)



(b)

Figure 3. The current–voltage (I-V) curve of nitrogen implanted TiO_2 sample. **(a)** without light; **(b)** with light illumination. The number in **(a)** and **(b)** is the measuring sequence.

Different from **Figure 3a,b** shows that there is a large hysteresis in the I-V curve when the sample is illuminated with a 60 mW laser. The current increases from 0 to 4326 μA when the bias voltage increases from 0 to 240 V. The current then decreases from 4326 μA to 661 μA when the bias voltage further increases from 240 to 250 V. The ratio of current peak to current valley is about 7. The I-V curve in the positive bias region is different from that in the negative bias region. So, it is not symmetric. In the negative bias region, the current increases to −1590 μA when the bias voltage is ramped up to −260 V. the current then decreases to −854 μA as the voltage is further increased to −270 V. The ratio of current peak to current valley is about 2. Therefore, this NDR is not repeatable and reduces quickly. It is evidently seen that light illumination plays an important role in NDR. The large number of photo-generated charge carriers and the enhanced polarization of $BiFeO_3$ were thought to be responsible for the NDR and RS [12]. The light-enhanced NDR was also reported in MoS_2 quantum dots sample [20]. The electric field to induce NDR in our sample with the assistance of light is about 1.25×10^3 V/cm. This is about three orders smaller than that reported [19]. There is a large reduction in electric field with the assistance of light. This behavior was not reported in the previous literatures [20].



(a) **(b)**

Figure 4. The NDR of sample kept at different humidity environment. **(a)** with 45% RH; **(b)** with 24% RH. The black and red curves are the first and second cycle measured I-V curves, respectively.

Figure 4 shows the NDR of sample kept at different humidity environment, respectively. As seen in **Figure 4**, the NDR in our sample is sensitive to the environment moisture. The NDR is largely recovered when the sample was kept in wet air with a humidity of 45% RH for about 5 days (**Figure 4a**). The ratio of current peak to the current valley is about 2.3. There is large hysteresis in the I-V curve obtained at the first bias voltage changing cycle (0 → 350 → 0→ −350 → 0 V). The hysteresis in the I-V curve becomes very weak in the second voltage changing cycle. In the other hand, the NDR is a little recovered when the sample was kept in dry air with a humidity of about 24% RH for 5 days. The current peak to valley ration is only about 1.3. The I-V curve in **Figure 4b** is almost similar for the two bias voltage changing cycles. The I-V curve in **Figure 4b** is almost similar for the positive bias

region and the negative bias region. In one voltage changing cycle, the bias voltage varies from 0→ 400 → 0 → −400 →0 V. The difference in I-V curve measured in different humidity means that atmosphere plays important role in NDR of nitrogen implanted TiO_2. This behavior is similar as that reported in literature [13].

Figure 5 shows the current (I) as a function of voltage (U) in the higher field region. As seen in **Figure 5**, in the higher field region, the logarithmic of I/U is proportional to the 1/U, i.e., $\ln(I/U) \propto 1/U$. This behavior is the character of metal-insulator granular films at high electric field region where the current is dominated by field induced tunneling [21]. In the case of our sample, the nonconductive fully-oxidized phase of titanium oxides (TO) plays the role of insulator. The water and conductive oxygen-deficient phase of titanium oxides (TO_x) can play the role of metal grains. It was thought that large amount of hydrogen ions can emerge from the ionization of water molecules to create electric current [13]. These conducting grains are randomly distributed and separated by insulator TO barrier. The current carriers transport by tunneling through the insulating barrier separating the conducting grains. This tunneling mechanism is hold in all cases (with light illumination or without light illumination. Before NDR or after NDR). The changing from TO_x to TO would increase the thickness of tunneling barrier and further reduce the tunneling current. On the contrary, the changing from TO to TO_x would decrease the thickness of tunneling barrier and further increase the tunneling current. The desorption (adsorption) of water would also increase (decrease) the tunneling distance and further lead the reduction (enhancement) of tunneling current.

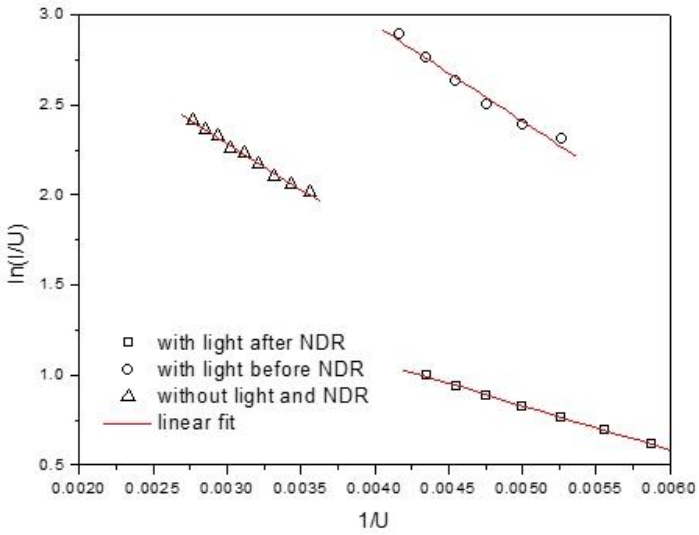


Figure 5. The dependence of Ln (I/U) on 1/U in the higher field region.

Based on the above experiments, the mechanism of NDR of nitrogen implanted TiO_2 should be partly related to the environmental moisture. Water molecular would be adsorbed in the nitrogen implanted TiO_2 sample [13]. With light illumination, a lot of electrons and holes are generated by photo. Some of the photo generated electrons and holes will migrate to the surface of sample, while others are recombined. Under the influence of electrical filed, the generated electrons and holes are further separated by large enough electric field and transport so that the current increases rapidly under a certain electrical filed. Large Joule heat will be generated in the case

of large current. The water molecular will be destroyed by Joule heat and the current is decreased [13]. Once the water is destroyed, there need a time period for water adsorption until the water is recovered again. Therefore, the I-V curve is not symmetrical and not repeatable in wet environment. In addition, the light illumination not only generates electron and hole pairs but also the photo catalyst effect. The photo catalyst can destroy water by changing water molecular into hydrogen and oxygen gas.

Besides the effect of moisture, the oxygen molecular and oxygen vacancy should also be considered. As shown in equation (1), the oxidation of lattice oxygen (O_o^x) and the formation of oxygen vacancies (V_o) in the vicinity are possible [14,22]. This reaction leaves behind two electrons and oxygen vacancy. The generated oxygen vacancies can migrate to form the conductive filaments. This further leads the increasing of electric current. In the reverse reactions, electrons and oxygen vacancy can be reduced and leading the reduction of current [22]. In the other hand, the electron can be scavenged by the adsorbed O_2 and produce adsorbed O_2^- [14]. The photo catalyst can also scavenge the current carriers by producing radicals such as H_2O•, OH•, and O_2•[17].

$$O_o^x \leftrightarrow V_o + 2e + \frac{1}{2}O_2 \tag{1}$$

With light illumination and nitrogen doping, it is advantage not only for the exciting of electron and hole, but also for the scavenging of electron [1]. Irradiation under vacuum with light selectively promotes electrons from nitrogen atom impurities to the conduction band according to the following process (2) and (3) [1].

$$N \xrightarrow{h\nu} N^+ + e \tag{2}$$

$$N^- \xrightarrow{h\nu} N + e \tag{3}$$

On the other hand, the presence of oxygen in the gas phase modifies the situation as a fraction of photo excited electrons is scavenged by O_2 producing adsorbed O_2^-(process (4) and (5)) [1].

$$N^- + O_{2(gas)} \xrightarrow{h\nu} N + O_{2(surf)}^- \tag{4}$$

$$N + O_{2(gas)} \xrightarrow{h\nu} N^+ + O_{2(surf)}^- \tag{5}$$

The nitrogen atom impurities exist either as charged centers (N^-) or as neutral centers (N) in TiO_2 [1]. Under the light irradiation with an energy of hν, electrons are promoted from the localized N-impurity states (N^- and N) to the electron scavengers like O_2 in environment ($O_{2(gas)}$). Then the O_2 in environment becomes negative charged and adsorbed on the surface ($O_{2\,(surf)}^-$). The electric current will be reduced by these electron scavengers. Furthermore, the surface adsorbed O_2^- will heal the defect sites such as oxygen vacancies and Ti^{3+} interstitials [23]. This will lead non-stoichiometric TiO_{2-x} transform to the stoichiometric insulating state, resulting in the NDR effect [11]. The surface oxidation can be reversed by local reduction [11]. The NDR due to surface oxidation should be reversible and repeatable.

4. Conclusion

In summary, with the assistance of visible light illumination, a negative differential resistance (NDR) with small electric filed (~1250 V/cm) and a large peak to valley ratio (~7) is obtained in nitrogen implanted TiO_2 single crystal. The NDR is related to the environment moisture. In higher humidity environment, the ratio of current peak to current valley is higher. However, the NDR in higher humidity is not reversible because the diffusion of water in sample is not fast enough. The possible mechanism of transport and NDR is discussed. The NDR should be related to the nitrogen dopants and the visible light induced reaction such as the destroy of the adsorption water, the scavenging of electron, and the surface oxidation transform of non-stoichiometric TiO_{2-x} to stoichiometric insulating state.

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