

## Nanoscale electrostatic and electrochemical transistors in correlated oxides

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Functional Oxides with strongly correlated electrons show characteristic phenomena such as colossal magnetoresistance, metal-insulator transition, caused by strong coupling among spin, charge and orbital degrees of freedom. Among many correlated oxides, vanadium dioxide (VO<sub>2</sub>) is the prototypical material, possessing a dramatic resistance and magnetism changes between a metallic state with paramagnetism and an insulating state with non-magnetism induced by dimerized singlet spins of vanadium atoms around 340 K. This metal-insulator transition (MIT) can be induced by a variety of external stimuli, such as thermal variation, lattice strain and electric field [1]. Controlling of MIT by an electric field is especially expected toward the realization of Mott transistor. In this research, we fabricated VO<sub>2</sub> nano-wire channel-based field effect-transistors [2] with a side-gate-type, bilayer insulating gates, air-gap side gate type so as to discuss their modulation mechanism.

Fig. 1(a) shows planer type-FET device geometry, where VO<sub>2</sub> thin films were deposited on TiO<sub>2</sub> (001) substrate [3] and Al<sub>2</sub>O<sub>3</sub> (0001) substrate [4] by using a pulsed laser deposition technique and

formed as nanowire channel and side gate patterns with a variety of width through nanoimprint lithography method. The electrical transport measurement was conducted in dried N<sub>2</sub> to neglect electrochemical reaction. The change rate in resistance (defined as  $(R_{\text{off}}-R_{\text{on}})/R_{\text{off}}$ , where  $R_{\text{off}}$  and  $R_{\text{on}}$  is the resistance of off-bias and on-bias states, respectively) on Al<sub>2</sub>O<sub>3</sub> (0001) substrate is 0.4% at gate bias  $V_G = 30$  V, while the rate on TiO<sub>2</sub> (001) substrate is 4.5% (Fig. 1(b)), which is 10 times higher

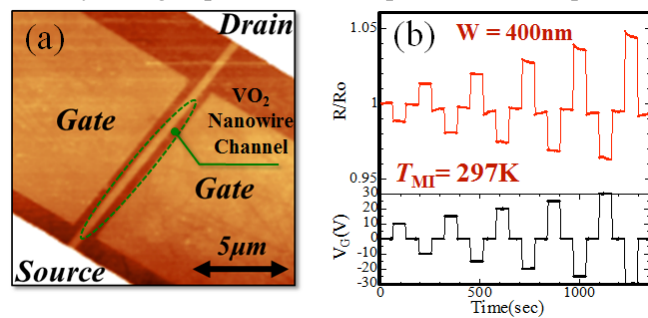


Fig. 1(a) AFM image of double side gate FET, (b) Time dependence resistance switch by applying gate bias for VO<sub>2</sub> nanowire channel on TiO<sub>2</sub> (001) substrate

than that using Al<sub>2</sub>O<sub>3</sub> (0001) substrate. It is considered that the huge difference was caused by obtaining single crystalline epitaxial VO<sub>2</sub> on TiO<sub>2</sub> (001) substrate. Furthermore, the change rate in resistance depend on wire width of VO<sub>2</sub> channels, that is, when reducing wire width of VO<sub>2</sub> channels from 3000 nm to 300 nm on TiO<sub>2</sub> (001) substrate, resistance modulation ratio enhanced from 0.7 % to 4.5 %. This indicated the advantage of nanowire and the modulation rate will be drastically enhanced in narrower width.

Next, epitaxial VO<sub>2</sub> nanowire-based FETs with high- $k$  inorganics Ta<sub>2</sub>O<sub>5</sub>/organic polymer parylene-C hybrid solid gate insulator [5-7] were prepared to enhance induced carrier density. In the typical device configuration, the width of VO<sub>2</sub> nanowire is 100 nm; the thickness of parylene-C is 80 nm; and the overlay Y-doped Ta<sub>2</sub>O<sub>5</sub> is of 250-nm-thick. Their change rate in resistance gradually increased at each given gate bias from 280 K to 295 K, which is close to the phase transition temperature, and suddenly became almost zero at 300 K in metallic state. The maximum value of resistance modulation is up to 8.58% for  $V_G = \pm 30$  V, near the phase transition temperature at 295 K. Fig. 2 plotted the

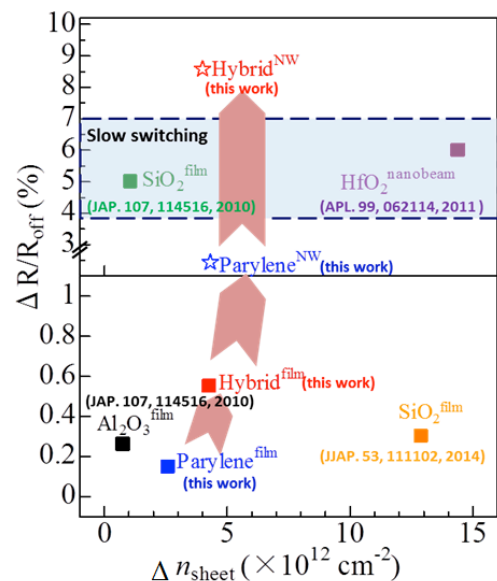


Fig. 2 Modulation efficiency VO<sub>2</sub>-based FETs with different solid gate insulators

resistance modulation efficiency for VO<sub>2</sub>-based FETs with various solid gate dielectrics reported as a function of the induced sheet carrier by gate dielectric  $\Delta n_{\text{sheet}}$  ( $\Delta n_{\text{sheet}}=C_i V_G/e$ ). Among these devices, the VO<sub>2</sub> nanowire-based FET with the hybrid gate dielectric exhibits large resistance modulation despite lower sheet carrier density of approximately  $5 \times 10^{12} \text{ cm}^{-2}$ , compared with other solid state VO<sub>2</sub>-based FETs. [7-11]

As further investigation in the VO<sub>2</sub> nano channel FET, dramatic transport changes were demonstrated by electric field-induced hydrogenation at room temperature through the nanogaps separated by humid air in a field-effect transistor structure with planar-type gates. Fig 3 shows the reversible, non-volatile resistance changes in a VO<sub>2</sub> nanowire channel with a width of 500 nm obtained by applying positive and negative  $V_G$  at 300 K under a humidity of around 50%. The normalized resistance ( $R/R_0$ , where  $R$  and  $R_0$  are the measured resistance and resistance of the pristine device before applying a  $V_G$  at 300 K, respectively) slowly decreased down to the saturation line at roughly  $R/R_0 = 0.75$  during the application of  $V_G = +100$  V. This state was held after the removal of the  $V_G$ . Namely, the device exhibited a non-volatile memory effect. Thus, the origin of the slow decrease in resistance under humid air conditions is probably not caused by mechanical relaxation or slow trapping from an electrostatic effect but by electrochemical reaction with intercalated H<sup>+</sup>, [12,13] which can substantially lower the resistivity in systems with sensitive 3d orbitals. With increasing  $V_G$ , electrolysis of the absorbed water starts over a threshold  $V_G$ , and H<sup>+</sup> are produced. After the intercalation of H<sup>+</sup>, strong H–O bonds are formed and electron transfer occurs from hydrogen onto the oxygen atom, changing the 3d-orbital occupancy of vanadium from V<sup>4+</sup> (3d<sup>1</sup>) to V<sup>3+</sup> (3d<sup>2</sup>) and resulting in dramatic transport modulation [14]. The electronic properties of transition metal oxides are quite sensitive to the orbital occupancy of electrons, and the valence numbers of transition metals are easily changed by redox reactions. Despite the slow modulation, the emergence of non-linear, plastic and/or memristive behaviors provides an opportunity to obtain new abilities in information processing [15], like signal flow in brain, in addition to electrostatic FET devices.

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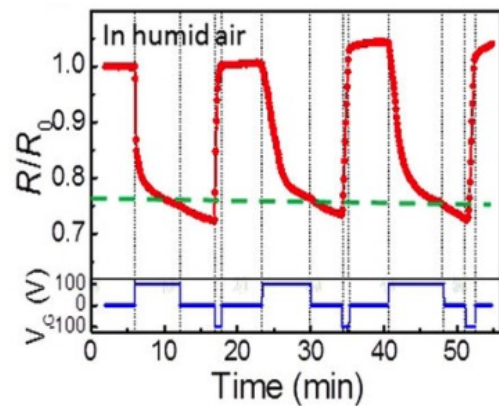


Fig. 3 Time dependence of the normalized resistance in VO<sub>2</sub> channel at 300 K with applied  $V_G$  values 100, 0 and -100 V in humid air.