Interface and surface electronic states of metal insulator materials studied across the transition forming Schottky interface with different Nb doping

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In this paper we review the case of two materials system namely VO$_2$(B) and NdNiO$_3$ which exhibits a metal insulator transition and makes a schottky junction with 0.01 and 0.5 wt % (100) Nb: SrTiO$_3$ substrates. The junction shows rectifying behavior all across the metal insulator transition (MIT). The current-voltage and capacitance characteristic shows no evidence of MIT. This indicates that the surface electronics of these materials is distinct from bulk and shows no bulk like transition.

The study of interface between two materials provides vital information about its electronic structure and the possibility of manipulation via electrical, thermal or magnetic means. Typical interfaces are of ohmic, tunnel or Schottky type and the applications based on this revolutionized modern electronics. For example, the electric field associated with a Schottky barrier can be used to drive electrons and holes in Solar cell. Schottky barrier between a known metal and an unknown semiconductor can be utilized to find the electronic structure of the semiconductor. Recently, heterointerfaces combining strongly correlated electron system attracted huge attention because of substantial electron reconstructions at the interface. Oxides interface electronic assembly may change considerably compare to their bulk counter part due to charge redistribution, along with e-e and e-lattice interaction at interface. The mechanism of electrical transport through interface can be complex but for most device concepts incorporating the diverse physical properties of these materials utilize interface barrier formation will be intriguing.

In this review, we are showing study of the interface electronic properties of VO$_2$(B)/Nb: SrTiO$_3$ and NdNiO$_3$/Nb: SrTiO$_3$ heteroepitaxial junctions using current-voltage and capacitance-voltage characteristics. The polymorph of VO$_2$ [referred to as VO$_2$(B)] was first described by Théobald et al.$^8$ VO$_2$(B) with C2/m(#12) space group; $a=12.093$ Å, $b=3.702$ Å, $c=6.433$ Å and $\beta=106.97^\circ$. Based on X-ray powder diffraction studies, Oka et al.$^9$ and others$^{10}$ have established that in bulk and nano rods of VO$_2$(B) the structural transition arises due to the formation of V$^{4+}$–V$^{4+}$ dimerization, though dimerization in this system is distinct from that observed in rutile VO$_2$. On the other hand NdNiO$_3$ belongs to the group of RNiO$_3$ pervoskite nickelate which undergoes the MIT at 200 K. The low temperature phase of NdNiO$_3$ is categorized as charge transfer insulating state.
The rectifying junctions have been shown using VO2(M)/Nb-TiO2 elsewhere.\textsuperscript{11,12} Whereas earlier work on bulk and nano beams of VO2(B) indicates that VO2(B) has metal to insulator transition as we cool VO2(B) to 150 K.\textsuperscript{9,13} VO2(B)’s layered structure makes it a promising material for its applications as electrode material for lithium batteries.\textsuperscript{14}

Heteroepitaxial junctions between VO2(B) films and NdNiO3 films are grown on 0.01 and 0.5 wt% Nb: SrTiO3(100) substrates using PLD. Fig. 1 (a) illustrates the resistivity versus temperature measurement in the range temperature from 150 K - 400 K for VO2(B) and VO2(M) and VO2(A) thin films. The VO2(M) shows a semiconductor to metal transition at around 340 K while the VO2(B) film shows a 4 orders of change in resistivity with large hysteresis in cooling and heating cycle.

![Graph showing temperature dependent resistivity](image)

**FIG 1.** Temperature dependent resistivity for (a) VO2(M) (90nm), and VO2(B) (20 nm, 90 nm and 120 nm thickness) films. (b) For NdNiO3 grown of different thickness.\textsuperscript{14,15}

The thickness dependent resistivity of VO2(B) depicts that for lower thickness, because of clamping effect from the substrate, the films show high resistivity at 300 K. It tells that the surface of VO2(B) is nominally metallic at all temperatures. They also confirmed ohmic junction characteristic of silver epoxy pasted as top contact on films and Al metal also making an ohmic contact to the top of the Nb-SrTiO3 substrate. On the other hand the NdNiO3 films of various thickness have been grown using PLD technique on 0.01 and 0.5 % Nb-STO substrate as shown in Figure 1b. The resistivity of the NdNiO3 film is normalized by the thickest film at 300 K for comparison. The thickness dependent resistivity data suggest the loss of MIT reduction in dynamical change in resistivity with reduced thickness.

The I-V measurements at various temperature for VO2(B) / 0.01 wt % and 0.5 wt % Nb-SrTiO3 junctions are shown Figs. 2 (a) and 2(b). The inset of Fig. 2 (a) is the devices structure. Positive voltage on VO2(B) films are considered as forward bias. The 1/C^2–V strategy have been used as shown in Fig. 2 (c) and (d) to estimate flat band voltages for VO2(B) / 0.01 wt % and 0.5 wt % Nb-SrTiO3 junctions. The intercepts on the Voltage- axis in the range of 0–0.5 V is used to calculate the flat band voltages of the junction.
The thermionic emission and tunneling current constitutes the total current in the Schottky device. The thermionic emission current and the capacitance of a Schottky junction devices can be stated as Eq. 1 & Eq. 2.\textsuperscript{16-20}

\[ I = A A^* T^2 \exp(-\beta \Phi_B) \exp\left[\frac{\beta(V-I_R)}{n}\right] \]  \hspace{1cm} (1)

\[ \frac{1}{C^2} = \frac{2}{q \varepsilon_0 \varepsilon_s N_D} (V_{bi} - V) \]  \hspace{1cm} (2)

Where, $\Phi_B$ = barrier height, $A^*$ = Richardson constant, $m^*$ = effective mass, $A$ = area, $R$ = series resistance, $\beta = q/kT$, $n$ = Ideality factor, $k$ = Boltzmann constant, $\varepsilon_s$ = dielectric constant, $N_D$ = dopant concentration, and $V_{bi}$ = built-in potential.

The Schottky barrier height is related to work functions of metal and semiconductor, the trapping of the Fermi level, and field penetration.\textsuperscript{21} The nonlinear and asymmetric behavior of $I$-$V$ curves in Fig. 2 (a), (b) suggests the rectifying behavior. The estimated ideality factor $n$ increases from ‘2’ to large values as we move from high to low temperature for junction 0.01 wt % Nb-SrTiO$_3$.

**FIG 2.** Temperature dependent $I$–$V$ characteristics of (a) VO$_2$(B)/0.01 wt % Nb-SrTiO$_3$ and (b) VO$_2$(B) / 0.5 wt% Nb: SrTiO$_3$. $1/C^2$–$V$ characteristics of (c) VO$_2$(B) /0.01 wt% Nb: SrTiO$_3$ and (d) VO$_2$(B) /0.5 wt% Nb: SrTiO$_3$.\textsuperscript{14}
The calculated reverse breakdown voltage in these result is -19 V and -16 V for VO₂(B) / 0.01 wt % and 0.5 wt % Nb-SrTiO₃ Schottky junctions respectively which can be related to the sensitivity of avalanche breakdown effect.²¹,²² These effects are also observed for Au/Nb-SrTiO₃ junctions.²³

Built-in potential $V_{bi}$ change with temperature for the VO₂(B) /Nb: SrTiO₃ junctions calculated from Fig. 2(c) and 2(d) for $T\downarrow$ (circle) and $T\uparrow$ (square). Fig. 3b. The built in potential of the NdNiO₃ /Nb: SrTiO₃ junctions.¹⁵

The barrier height $V_{bi}$ is estimated using Eq. 2 and fitting it to the data in Fig. 2 (c) & (d) from 0 V-0.5 V as plotted in Fig. 3 (a) at various temperature upto 160 K. The change in barrier height is small for VO₂(B) / 0.5 wt % Nb-SrTiO₃ junction because in the VO₂(B) / 0.5 wt % Nb-SrTiO₃ junction. This effect arises due to the relative decrease in depletion region at the interface to the junction capacitance as the Nb concentration increases. For higher Nb concentration the large internal electric field at the junction pushes the large εₛ, which is comparatively temperature independent thus making $V_{bi}$ less temperature sensitive.²⁴,²⁵ However, gradual increases in $V_{bi}$ through the metal-to-insulator transition in Fig. 3a-3b without any hysteresis suggests that the electronic structure of VO₂(B) at the interface is unaffected. Fig. 3 (b) shows the temperature dependence of the built-in potential $V_{bi}$ of the NdNiO₃/Nb: SrTiO₃ junctions, which indicates no change in electronic structure at the interface of NdNiO₃ and Nb-STO substrate very similar to the VO₂(B) case. Hence substrate clamping effect suppress the electronic phase transition in these material system at the interface.
The depletion width dependence on the doping concentration at zero bias can be expressed as Eq. 3

\[
W_{\text{dep}} = \sqrt{2\varepsilon_{\text{s}} \left( \frac{V_{\text{bi}}}{qN_D} \right)}
\]

Using \(N_D, \varepsilon_s\) from references\(^{25,26}\) and \(V_{\text{bi}}\) from Fig. 3 (a), it shown that the depletion width comes ~80 nm for VO\(_2\)(B)/ 0.01 % Nb-SrTiO\(_3\) and 8 nm for VO\(_2\)(B)/ 0.5 % Nb-SrTiO\(_3\) Schottky junction.\(^{14}\)

In the junctions, above \(T_{\text{MI}}\) a Schottky contact would be expected between metallic phase and the \(n\)-type semiconductor Nb-SrTiO\(_3\), as illustrated in Fig. 4a. Crossing the MI transition should induce a hysteretic change in the junction current-voltage (\(I-V\)) characteristics, in part arising from a shift in the chemical potential in transition metal oxide material system, as well as decrease in the junction capacitance \(C\), reflecting the opening of the gap, as illustrated in Fig. 4b. Instead, experimentally it is seen that junctions shows rectifying behavior at all temperatures. Any change in the interface electronic structure of transition metal oxide materials such as VO\(_2\)(B) and NdNiO\(_3\) is not observed across \(T_{\text{MI}}\). This shows that the surface of both VO\(_2\)(B) and NdNiO\(_3\) is metallic at all temperatures, consistent with the suppression of the MI transition with decreasing film thickness.

In conclusion this review suggests a suppression of MI transition at the schottky interface of transition metal oxides such as VO\(_2\)(B) and NdNiO\(_3\) with Nb-STO, which is also supported by the fact that \(T_{\text{MI}}\) suppresses with film thickness decrease. We further conclude that opposite to heterostructures having insulating dead layer at the interface, in these metal insulator transition material/Nb-STO interfaces, the substrate clamping effect
freezes the higher symmetry phase of the thin films at the interface and thus prevents the MI transition in metal insulator transition materials.

References: