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# Insights into the interfaces of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) polymorphs with different substrates

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The phenomena arising at the interface between oxide materials and substrates can fundamentally and practically change the physical and chemical properties of the materials themselves. In this study, we employed density functional theory (DFT) calculations to elucidate the stability and optical properties of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) interactions with substrates of sapphire(c-cut), sapphire(r-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), SrNbO<sub>3</sub>(001), SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(c-cut), and LaAlO<sub>3</sub>(r-cut). The surface calculations showed that the fully relaxed SrTiO<sub>3</sub>(111) and SrNbO<sub>3</sub>(001) possess the highest energies of 31.8 eV nm<sup>-2</sup> and 21.15 eV nm<sup>-2</sup> relative to other slabs, before optimizing with VO<sub>2</sub>(M) and VO<sub>2</sub>(B) polymorphs, respectively. The calculated adsorption energy indicated that the interface of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) structures showed more stability on SrTiO<sub>3</sub>(001) and SrTiO<sub>3</sub>(111), with adsorption energy values of 2.83 eV and 0.91 eV, respectively. Furthermore, the optical absorption properties of the highest and lowest stable interfaces have been evaluated. The outcomes predicted that VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) have their optical adsorption in the visible light range, while VO<sub>2</sub>(M)@sapphire(c-cut) and VO<sub>2</sub>(B)@sapphire(c-cut) showed the main adsorption peak in the infrared region.

## Introduction

Epitaxial synthesis of heterostructure oxides has shown considerable promise in creating new functionalities and chemical-physical properties by controlling some parameters, such as lattice, spin, charge, and orbital order.<sup>1</sup> Heterostructures of oxide materials allow for tuning the electronic, magnetic, and optical properties, as well as giving rise to emergent behaviours that are distinct from the bulk properties of either material. Since there are no substrates available with similar structures (lattice parameters and crystal symmetry), the ability to grow the thin films of binary oxides like TiO<sub>2</sub><sup>2</sup> and VO<sub>2</sub><sup>3,4</sup> on lattice- and symmetry-mismatched substrates is of crucial importance for discovering their unprecedented potential.

It is well known that vanadium oxides (VO<sub>2</sub>) represent an abundant and diverse family of compounds with multipurpose applications. VO<sub>2</sub> exists in multiform polymorphic stable and metastable forms, including rutile VO<sub>2</sub>(R),<sup>5</sup> monoclinic VO<sub>2</sub>(M),<sup>6</sup> and triclinic VO<sub>2</sub>(T) phases,<sup>7</sup> that are similar in structure. But there are other four VO<sub>2</sub> phases designated as tetragonal VO<sub>2</sub>(A),<sup>8</sup> monoclinic VO<sub>2</sub>(B),<sup>9</sup> paramontroseite VO<sub>2</sub>,<sup>10</sup> and VO<sub>2</sub> with a new body centered-cubic (bcc)

structure.<sup>11</sup> Among them, VO<sub>2</sub>(M) possesses a fully reversible metal-insulator phase transition to the most stable VO<sub>2</sub>(R), associated with the benefits of huge temperature-induced resistivity changes as well as the selective optical switches, which have received great interest in industrial and scientific areas for construction of intelligent devices such as temperature sensors,<sup>12</sup> GHz operating frequency,<sup>13</sup> thermochromics,<sup>14</sup> and energy efficient smart windows.<sup>14</sup> On the other hand, the VO<sub>2</sub>(B) phase has also been explored as a promising cathode material in Li-ion batteries, not only on the basis of its appropriate electrode potential, but also its particular tunnelled structure.<sup>15</sup> However, metastable VO<sub>2</sub>(B) is a relatively less-studied polymorph in comparison to the other oxides of vanadium.

Recently, our group has carried out a comprehensive DFT-study on the characterization of the geometry, stability, Raman spectra, and the electronic, magnetic, and optical properties of VO<sub>2</sub>(M)<sup>16</sup> and VO<sub>2</sub>(B)<sup>17,18</sup> nanostructures. The study on the electronic band gap of VO<sub>2</sub>(M)<sup>16</sup> based on the Heyd-Scuseria-Ernzerhof (HSE)<sup>19</sup> functional showed excellent agreement with photoemission experiments (band gap ~ 0.6–0.7 eV)<sup>20</sup> by a band gap of 0.6 eV. In addition to the improved prediction of the peak position in the absorption spectra with the same functional, this method also described reasonably well the static dielectric constant of 7.54 of VO<sub>2</sub>(M), showing an excellent match with the experimental values. In an experimental work by Lourembam *et al.*,<sup>21</sup> they have investigated the photo-induced insulator-to-metal transition in VO<sub>2</sub>(B) using the

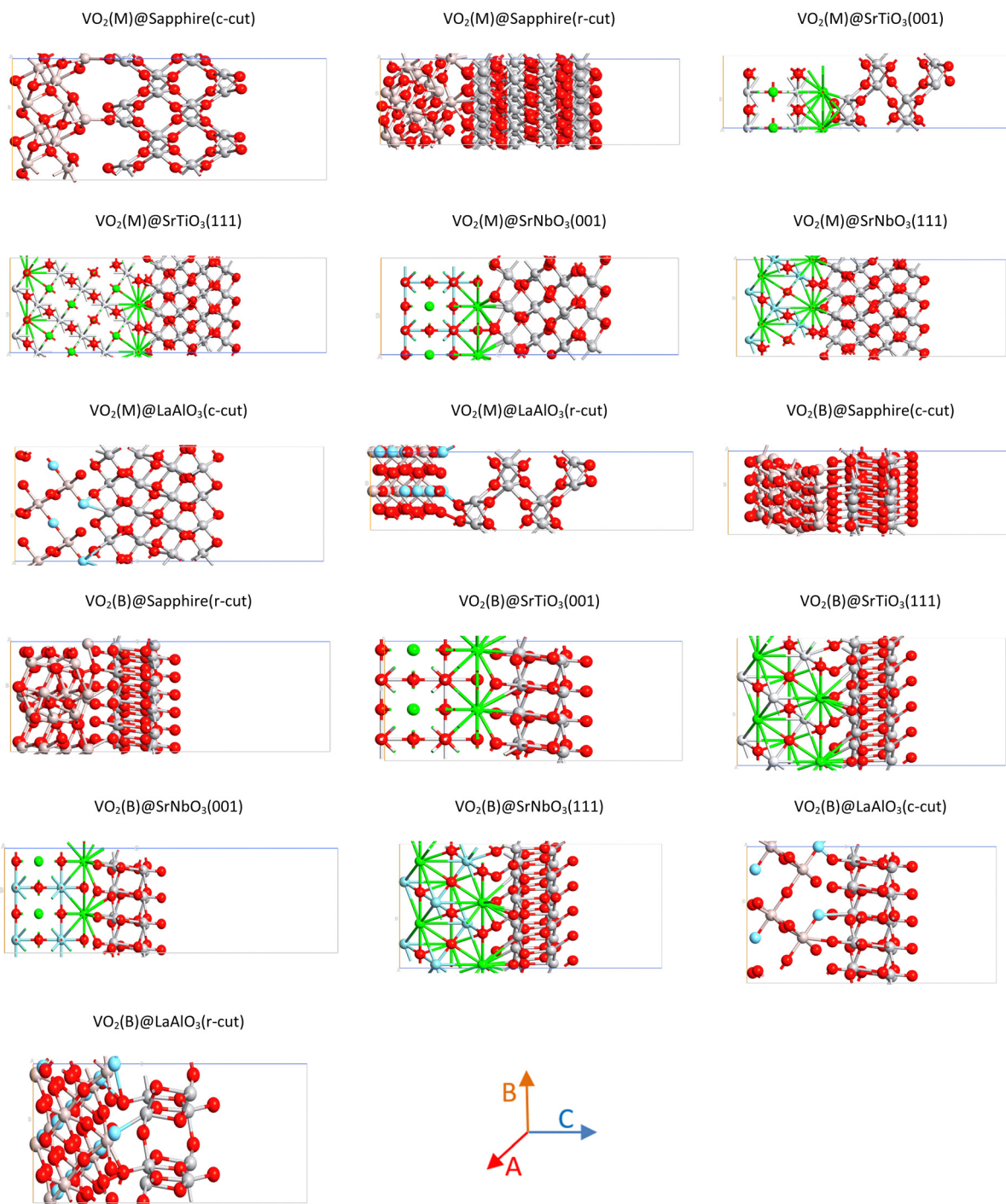
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temperature-dependent optical pump-probe technique. This study reported the metallic phase (300 K) and the insulating phase (100 K) of this structure, respectively; however, the insulating phase can be indicated by two electronic relaxation times and the metallic phase showed only one characteristic time. Our recently study<sup>17</sup> based on the use of PBEsol<sup>22</sup> demonstrated for the first time the experimental metallic-like phase of VO<sub>2</sub>(B).

So far, using pulsed laser epitaxy (PLE), high quality VO<sub>2</sub>(M) and VO<sub>2</sub>(B) thin films were successfully stabilized on perovskite substrates like SrTiO<sub>3</sub>. Chen *et al.*<sup>23</sup> reported that the textured VO<sub>2</sub>(B) thin film with a layered structure was grown on SrTiO<sub>3</sub>(001) by pulsed laser deposition. In addition, a small amount of the VO<sub>2</sub>(M) phase can co-grow in the VO<sub>2</sub>(B) phase. This study indicates an alternative approach to enhance the performance of insulating VO<sub>2</sub>(B) based batteries by increasing



**Fig. 1** Schematic representations of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) material interfaces with different substrates. The color code in the ball and stick models: V grey, O red, Al pink, Sr green, Nb cyan, Ti silver, and La light blue.



the electrical conductivity. Srivastava *et al.*<sup>24</sup> demonstrated the novel heterostructures of high-quality single-phase films of VO<sub>2</sub> (A and B) on the SrTiO<sub>3</sub> substrate by controlling the vanadium arrival rate (laser frequency) and oxidation of the V atoms. In addition, the *c*-plane Al<sub>2</sub>O<sub>3</sub> (sapphire) substrate has been used to consider the first phase transition stability of VO<sub>2</sub> thin films grown *via* both *ex situ* heating and *in situ* heating by transmission electron microscopy (TEM). Electrical resistance measurements were conducted on the VO<sub>2</sub> thin films to characterize the semiconductor to metallic transition (SMT) properties during multiple thermal cycles. *In situ* TEM heating experiments were conducted to investigate the film microstructure evolutions during phase transition cycles.<sup>25</sup>

In this work, using DFT calculations, for the first time, we reported the stability and optical properties of different interfaces of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) on sapphire(*c*-cut), sapphire(*r*-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), Nb substituted with Ti in SrNbO<sub>3</sub>(001) and SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(*c*-cut), and LaAlO<sub>3</sub>(*r*-cut) surfaces and used these results to understand how two dissimilar materials can form heterostructures with different characterizations. Computational advances in the atomic-scale simulations of oxide heterostructures are able to provide a fertile new ground for creating novel states at their interfaces and varied symmetry constraints can be used to design structures exhibiting phenomena that are not found in the bulk constituents and then that can be exploitable in practical device applications of VO<sub>2</sub>.

## Results and discussion

Initially, the slab of various configurations was modelled; then, different interfaces, as seen in Fig. 1, were constructed by the interactions between the slabs and the VO<sub>2</sub>(M) and VO<sub>2</sub>(B) perpendicular to the surface along the *z* direction. All the information related to the crystal structure and lattice parameters for substrates of Al<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub> and LaAlO<sub>3</sub> as well as VO<sub>2</sub>(M and B) polymorphs are reported in Table 1. Moreover, the details related to the lattice dimensions for different interfaces are reported in Table 2. It is evident from our computational results that after the structural relaxation of all supercells, the vertical distances between VO<sub>2</sub> (M and B) and different facets of SrTiO<sub>3</sub> and SrNbO<sub>3</sub> are lower (an average interface distance of 2.37 Å) than those for Al<sub>2</sub>O<sub>3</sub> and LaAlO<sub>3</sub> substrates. The outcomes indicate that the adsorption is primarily dominated by the vdW interactions on the substrates of sapphire facets and even in La-containing slabs, with vertical

**Table 1** Crystal structure and lattice parameters for substrates and VO<sub>2</sub> (M and B) polymorphs

Bulk systems	Crystal structure (space group)	Lattice constant			
		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)
Al <sub>2</sub> O <sub>3</sub>	Trigonal ( <i>R</i> $\bar{3}C$ )	4.81	4.81	13.12	120
SrTiO <sub>3</sub>	Cubic ( <i>Pm</i> $\bar{3}m$ )	3.95	3.95	3.95	90
LaAlO <sub>3</sub>	Trigonal ( <i>R</i> $\bar{3}C$ )	5.41	5.41	13.19	120
VO <sub>2</sub> (M)	Monoclinic ( <i>P2</i> <sub>1</sub> / <i>c</i> )	5.38	4.52	5.74	122.6
VO <sub>2</sub> (B)	Monoclinic ( <i>C2</i> / <i>m</i> )	12.03	3.69	6.42	106

**Table 2** Lattice dimensions for different interfaces of VO<sub>2</sub>(M and B) polymorphs

Interface	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)
VO <sub>2</sub> (M)@sapphire( <i>c</i> -cut)	9.61	10.35	21.61	62.35
VO <sub>2</sub> (M)@sapphire( <i>r</i> -cut)	18.34	7.06	21.07	118.11
VO <sub>2</sub> (M)@SrTiO <sub>3</sub> (001)	11.15	7.89	23.29	45
VO <sub>2</sub> (M)@SrTiO <sub>3</sub> (111)	11.15	11.15	22.27	60
VO <sub>2</sub> (M)@SrNbO <sub>3</sub> (001)	11.15	7.89	20.27	45
VO <sub>2</sub> (M)@SrNbO <sub>3</sub> (111)	11.15	11.15	24.07	60
VO <sub>2</sub> (M)@LaAlO <sub>3</sub> ( <i>c</i> -cut)	10.82	10.78	22.62	120.112
VO <sub>2</sub> (M)@LaAlO <sub>3</sub> ( <i>r</i> -cut)	23.55	5.39	22.31	90.26
VO <sub>2</sub> (B)@sapphire( <i>c</i> -cut)	17.35	11.06	20.01	15.25
VO <sub>2</sub> (B)@sapphire( <i>r</i> -cut)	16.94	7.71	22.30	95.36
VO <sub>2</sub> (B)@SrTiO <sub>3</sub> (001)	11.83	7.89	18.39	90
VO <sub>2</sub> (B)@SrTiO <sub>3</sub> (111)	12.51	11.15	19.43	120
VO <sub>2</sub> (B)@SrNbO <sub>3</sub> (001)	11.83	7.89	28.92	90
VO <sub>2</sub> (B)@SrNbO <sub>3</sub> (111)	11.15	11.15	19.07	120
VO <sub>2</sub> (B)@LaAlO <sub>3</sub> ( <i>c</i> -cut)	10.82	10.78	17.42	59.88
VO <sub>2</sub> (B)@LaAlO <sub>3</sub> ( <i>r</i> -cut)	17.85	10.78	16.87	41.24

distances around 3.63 Å. By considering the chemical properties of different elements like electron configuration, atomic radius and electronegativity, as shown in Table 3, since the vanadium (V) atom has a small atomic radius of 134 pm and an electronegativity of 1.63, the charges can transfer more easily with strontium (Sr), having an electronegativity of 0.91 and a bigger radius sphere of 255 pm, compared to aluminium (Al) with a similar electronegativity of 1.61 and an atomic radius of 143 pm. When we used the SrNbO<sub>3</sub> and LaAlO<sub>3</sub> substrates, still we get the direct connections of Sr–V and Al–V in the interfaces, and the chemical properties of Nb and La atoms could not significantly affect the chemical properties of vanadium atoms. The comparison between titanium (Ti) (niobium (Nb)) in SrTiO<sub>3</sub> (SrNbO<sub>3</sub>) substrates indicates that the charges can transfer more easily with titanium (Ti), having an electronegativity of 1.54 and a smaller radius sphere of 187 pm, compared to Nb with a similar electronegativity of 1.60 but a bigger atomic radius of 207 pm. The same condition exists for the La atom in LaAlO<sub>3</sub> which has a bigger atomic radius (250 pm) than Al (143 pm). However, as we see later, the presence of these elements can influence less the stability of heterostructures.

After simulating all interface systems, we removed VO<sub>2</sub>(M) and VO<sub>2</sub>(B) polymorphs from the supercells and we evaluated the surface energy of different relaxed surfaces. The theoretical formalism for evaluating the surface energy can be expressed from the following formula:<sup>26</sup>

**Table 3** Chemical properties of different elements in materials

Element	Electron configuration	Atomic radius (pm)	Electronegativity
Sr(Ti, Nb)O <sub>3</sub>			
Sr	[Kr] 5s <sup>2</sup>	255	0.95
Ti	[Ar] 3d <sup>2</sup> 4s <sup>2</sup>	187	1.54
Nb	[Kr] 4d <sup>4</sup> 5s <sup>1</sup>	207	1.60
Al(Al, La)O <sub>3</sub>			
Al	[Ne] 3s <sup>2</sup> 3p <sup>1</sup>	143	1.61
La	[Xe] 5d <sup>1</sup> 6s <sup>2</sup>	250	1.10
VO <sub>2</sub>			
V	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	134	1.63



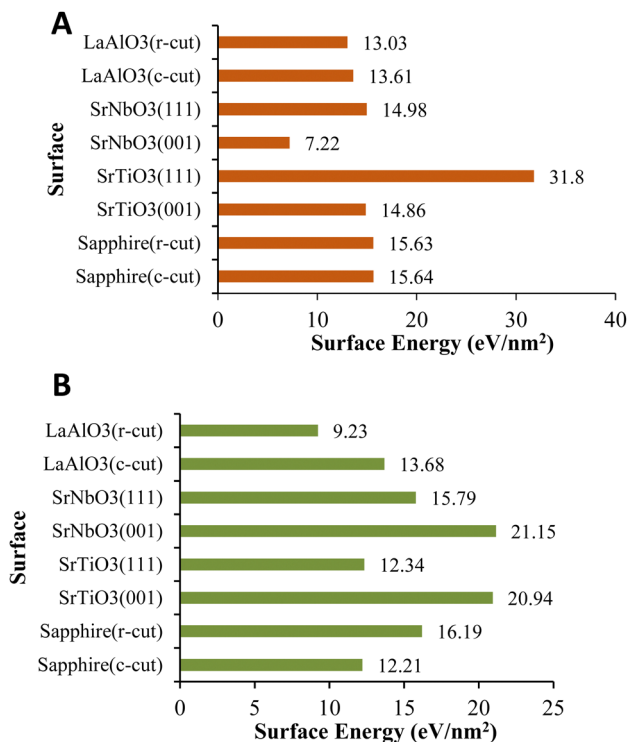


Fig. 2 Surface energy for relaxed different slabs of sapphire(c-cut), sapphire(r-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), SrNbO<sub>3</sub>(001), SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(c-cut), and LaAlO<sub>3</sub>(r-cut) before optimizing with VO<sub>2</sub>(M) (A) and VO<sub>2</sub>(B) (B) polymorphs.

$$E_s = E(n) + nE_{\text{Bulk}}/2A \quad (1)$$

where  $A$  is the area of the primitive surface unit cell,  $E(n)$  refers to the energy of a slab with  $n$  formula units, and  $E_{\text{Bulk}}$  is the energy of a formula unit of the bulk material. The results of the present DFT calculations of the surface energy for different slabs are summarized in Fig. 2, where all the calculations are related to the fully relaxed slabs.

As can be seen, in the case of VO<sub>2</sub>(M), the surface energy of fully relaxed SrTiO<sub>3</sub>(111) is considerably larger than all the slabs with 31.8 eV nm<sup>-2</sup>; however, the surface energy of sapphire(c-plane) has a similar magnitude to those of sapphire(r-plane), SrNbO<sub>3</sub>(111), and SrTiO<sub>3</sub>(001) by values of 15.65 eV nm<sup>-2</sup>, 15.63 eV nm<sup>-2</sup>, 14.98 eV nm<sup>-2</sup>, and 14.86 eV nm<sup>-2</sup>, respectively. The magnitude of the relaxed surface energies for SrNbO<sub>3</sub>(001) is lower than that for all the slabs with 7.22 eV nm<sup>-2</sup> and some middle surface energy values can be observed for LaAlO<sub>3</sub>(c-cut) (13.61 eV nm<sup>-2</sup>) and LaAlO<sub>3</sub>(r-cut) (13.03 eV nm<sup>-2</sup>). Inspections of Fig. 2 show that the surface energy of different interfaces with the VO<sub>2</sub>(B) polymorph assumed different values, in the order of SrNbO<sub>3</sub>(001) > SrTiO<sub>3</sub>(001) > sapphire(r-cut) > SrNbO<sub>3</sub>(111) > LaAlO<sub>3</sub>(c-cut) > SrTiO<sub>3</sub>(111) > sapphire(c-cut) > LaAlO<sub>3</sub>(c-cut) with the surface energies of 21.15 > 20.94 > 16.19 > 15.79 > 13.68 > 12.34 > 12.21 > 9.23 eV nm<sup>-2</sup>, respectively. Woo *et al.*<sup>27</sup> also concluded the surface energy of 28–34 eV nm<sup>-2</sup> of SrTiO<sub>3</sub>(111) as the most stable facet of SrTiO<sub>3</sub>. In fact, there is also reasonably good qualitative agreement with the theoretical

results of Stirner *et al.*<sup>28</sup> who obtain the relative surface energies of various sapphire surfaces with the ratios of 11–30 eV nm<sup>-2</sup> for the *c*-plane and 14–19 eV nm<sup>-2</sup> for the *r*-plane. It is also interesting to note from Fig. 2 that, amongst these different surface facets, *r*- and *c*-plane LaAlO<sub>3</sub> have shown the middle surface energy in good consistency with that shown in ref. 29 in which the surface energy of 5–29 eV nm<sup>-2</sup> is reported for the *c*-plane face of this substrate.

To find the most stable geometric configurations, we investigated the adsorption energy of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) on different surfaces (Fig. 3). We calculated the adsorption of different interfaces using the following eqn (2)<sup>30,31</sup>

$$E_{\text{ads}} = E_{\text{VO}_2(x)} + E_{\text{substrate}} - E_{\text{VO}_2(x)+\text{substrate}} \quad (2)$$

where  $E_{\text{substrate}}$  refers to the total energies of isolated VO<sub>2</sub> (M, or B) and substrates and  $E_{\text{VO}_2(x)+\text{substrate}}$  is the total energy of the interface system. Our data indicate that for VO<sub>2</sub>(M) adsorption, sapphire(c-cut) and sapphire(r-cut) exhibit similar binding energies of 31.76 eV and 30.52 eV, respectively, owing to its weak physical interaction with no chemical bond formation directly corroborating to its larger vertical distance to VO<sub>2</sub> polymorphs and the values are significantly lower than those of SrTiO<sub>3</sub>(001) (2.83 eV), SrTiO<sub>3</sub>(111) (6.69 eV), SrNbO<sub>3</sub>(001) (6.41 eV), and SrNbO<sub>3</sub>(111) (10.46 eV), LaAlO<sub>3</sub>(c-cut) (14.1 eV) and LaAlO<sub>3</sub>(r-cut) (11.92 eV). The adsorption energies of VO<sub>2</sub>(B) on the surfaces became stronger than those of VO<sub>2</sub>(M). According to our DFT calculations, the calculated binding energies are 21.12, 1.11, 4.14, 0.91, 8.02, 6.39, 19.10 and 5.49 for sapphire(c-cut), sapphire(r-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), SrNbO<sub>3</sub>(001), SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(c-cut), and LaAlO<sub>3</sub>(r-cut) surfaces, respectively. We observe that the most stable interfaces for VO<sub>2</sub>(M) and VO<sub>2</sub>(B) structures are

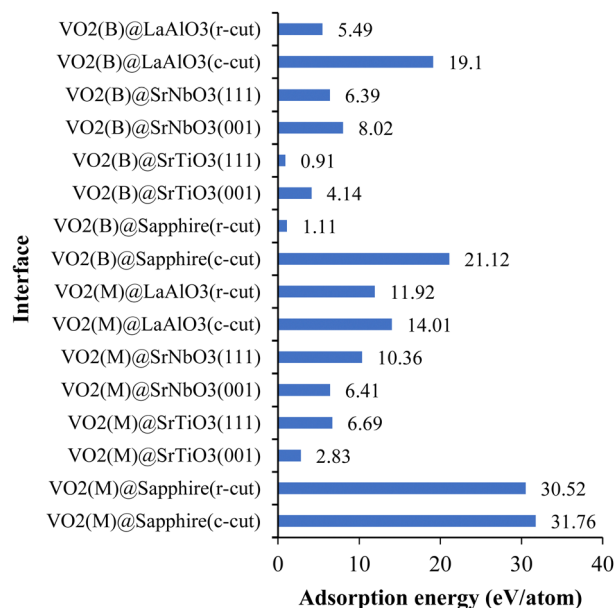


Fig. 3 Adsorption energy for different interfaces of VO<sub>2</sub>(M and B) polymorphs on sapphire(c-cut), sapphire(r-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), SrNbO<sub>3</sub>(001), SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(c-cut), and LaAlO<sub>3</sub>(r-cut) substrates.



SrTiO<sub>3</sub>(001) and SrTiO<sub>3</sub>(111), while the less stable interfaces are related to sapphire(*c*-cut) for both polymorphs.

### Optical properties

The absorption coefficients for VO<sub>2</sub>(M) and VO<sub>2</sub>(B) polymorphs on the VO<sub>2</sub>(M)@sapphire(*c*-cut), VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001), VO<sub>2</sub>(B)@sapphire(*c*-cut), and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) interfaces are plotted in Fig. 4, as the most (VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111)) and less (VO<sub>2</sub>(M)@sapphire(*c*-cut) and VO<sub>2</sub>(B)@sapphire(*c*-cut)) stable interfaces, as we discussed before. Here, we reported the acquired results in the visible (from 380 to 780 nm) and infrared (from 780 to 2500 nm) ranges as a function of wavelength. Based on this figure and the range of photon energy, the maximum absorption coefficients are  $28 \times 10^4 \text{ cm}^{-1}$  (at 500 nm) and  $21 \times 10^4 \text{ cm}^{-1}$  (at 620 nm) for VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) along the *xx* in-plane direction in the central energy zone of visible light (green–yellow) and low energy part of the visible light (red), respectively. The corresponding values predicted for VO<sub>2</sub>(M)@sapphire(*c*-cut) and VO<sub>2</sub>(B)@sapphire(*c*-cut) are  $24 \times 10^4 \text{ cm}^{-1}$  (at 1500 nm) and  $19 \times 10^4 \text{ cm}^{-1}$  (at 1000 nm), along the in-plane direction, respectively, with the

first main peaks of the absorption coefficient in the light infrared region of the electromagnetic spectrum.

We next discuss the dielectric constant of the four interfaces, as we assessed their optical adsorption. The real and imaginary parts of dielectric constant of VO<sub>2</sub>(M)@sapphire(*c*-cut)(A), VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001)(B), VO<sub>2</sub>(B)@sapphire(*c*-cut)(C), and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) (D) interfaces are presented in Fig. 5, as a function of energy (eV). The imaginary part of all interfaces began with a high intensity of VO<sub>2</sub>(M)@sapphire(*c*-cut) (A), while the intensity of peaks dropped with that of VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) (D). In addition, the optical edge, which is called the optical band gap, can be calculated for these systems by drawing a vertical line from the wall of the first peak to the horizontal *x*-axis and here the outcomes indicate that the optical band gap is zero in all cases. According to this study, a static real dielectric constant has its maximum values at 107, 76 and 36 along the *xx*-, *yy*- and *zz*-directions for VO<sub>2</sub>(M)@sapphire(*c*-cut) (A), while the corresponding values have reduced to 61, 43, and 11 for VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) (B) along the same directions, respectively. In comparison, VO<sub>2</sub>(B) interfaces showed a lower static dielectric constant than VO<sub>2</sub>(M) ones by 33, 22 and 12 for VO<sub>2</sub>(B)@sapphire(*c*-cut) (C) and the lowest

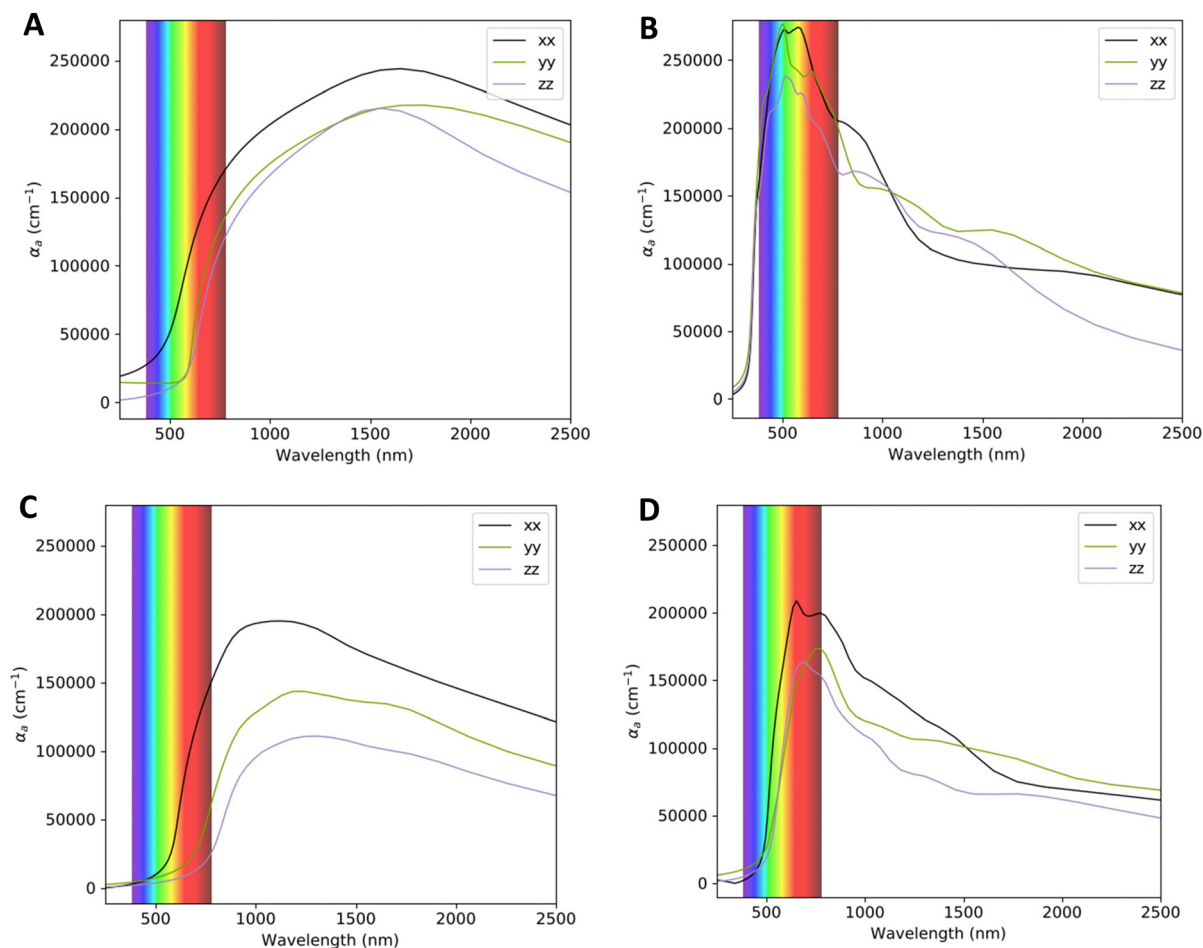


Fig. 4 Optical adsorption of VO<sub>2</sub>(M)@sapphire(*c*-cut) (A), VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) (B), VO<sub>2</sub>(B)@sapphire(*c*-cut) (C), and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) (D) interfaces, as a function of the wavelength (nm) scale.



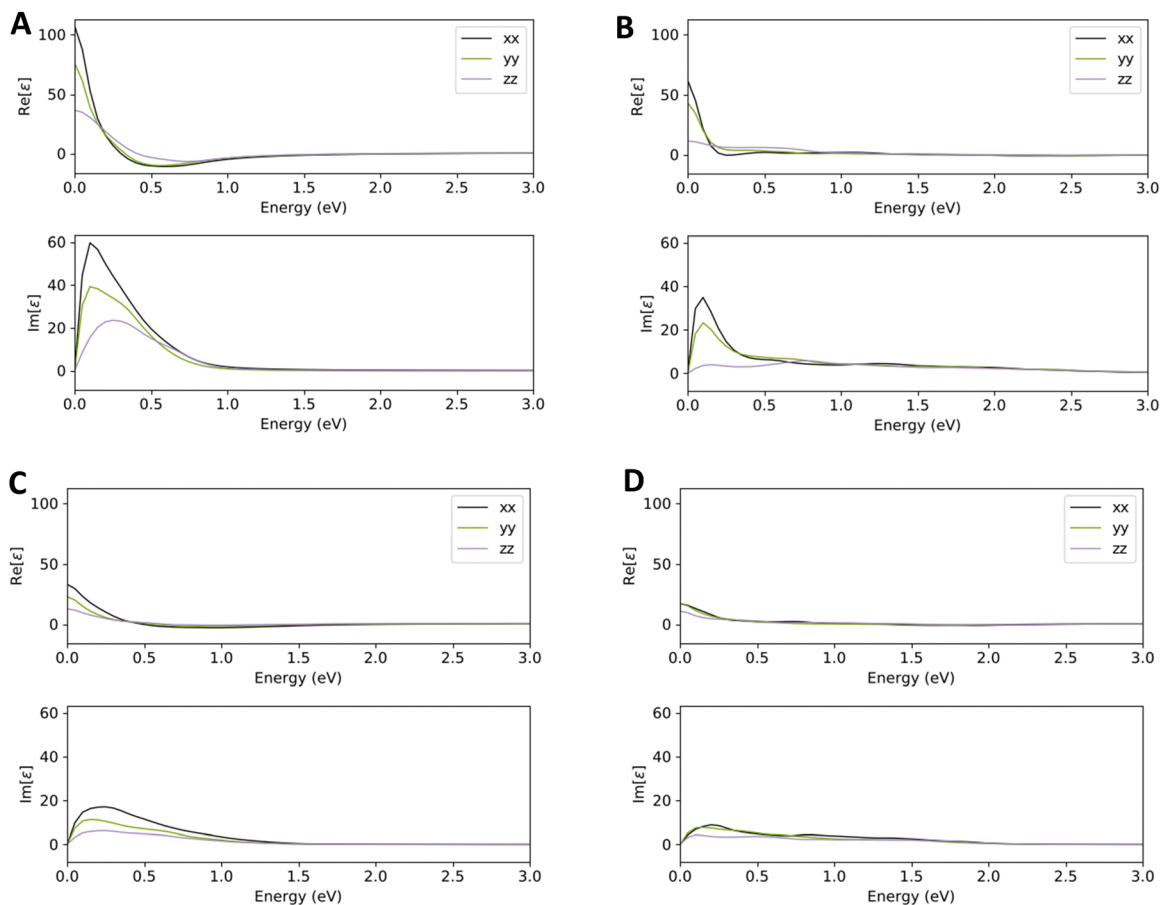


Fig. 5 Real and imaginary parts of dielectric constants of  $\text{VO}_2(\text{M})@sapphire(\text{c-cut})$  (A),  $\text{VO}_2(\text{M})@SrTiO_3(001)$  (B),  $\text{VO}_2(\text{B})@sapphire(\text{c-cut})$  (C), and  $\text{VO}_2(\text{B})@SrTiO_3(111)$  (D) interfaces, at energy (eV) scale.

values for  $\text{VO}_2(\text{B})@SrTiO_3(111)$  (D) with 17, 16 and 10 along the in-plane and out-of-plane directions, respectively. These theoretical advances in the optical adsorption and high dielectric constant further highlight the desirable performances of these proposed  $\text{VO}_2$ -based interfaces, suitable for photoelectronic applications such as solar energy conversion<sup>32,33</sup> and infrared light photodetectors<sup>34,35</sup> with high optical absorption in the visible and infrared regions, respectively.

According to the outcomes reported in the section “Results and discussion”, by optimization of all four systems, the vertical distances between  $\text{VO}_2(\text{M})/SrTiO_3$  and  $\text{VO}_2(\text{B})/SrTiO_3$  layers showed lower values with respect to  $\text{VO}_2(\text{M})/sapphire$  and  $\text{VO}_2(\text{B})/sapphire$  interfaces. These equilibrium distances between the layers can efficiently influence the electronic band diagram of the interfaces such as the density of the charges of each element in the valence and conduction band edges. Moreover, the calculated adsorption energy for each heterostructure is in the same trend with the geometrical parameter results which reveal more interaction between  $\text{VO}_2(\text{M})/\text{VO}_2(\text{B})$  with the  $SrTiO_3$  surface. It is worth to notice that all mentioned structural parameters and interface energies are induced by the large symmetry mismatch between the adsorbates and surfaces. On the other hand, while we observed the zero optical band gap for all four interfaces, the optical adsorption and

dielectric constant of each material as well as substrate can affect the optical features of the total interface. As reported by previous studies, the imaginary and real part of the dielectric constant of  $SrTiO_3$  shows the optical band gap in the visible range and a lower static dielectric constant<sup>36</sup> than sapphire with the infrared-active modes.<sup>37,38</sup> More interestingly, the formation of an interfacial layer composed of  $\text{VO}_2(\text{B})$  on  $SrTiO_3$  and sapphire by the larger symmetry mismatch (with respect to  $\text{VO}_2(\text{M})$  interfaces) showed a lower dielectric constant (as seen in Fig. 5) to facilitate the symmetry transition between the two distinct component structures.

## Methods

We carried out the atomistic calculations using the Quantum Atomistic ToolKit (QATK)<sup>39</sup> package. The DFT approach was implemented in the Kohn–Sham (KS) formulation,<sup>40</sup> within the framework of the linear combination of atomic orbitals (LCAO) basis set approach, combined with the pseudopotential (PPs) method and the Perdew–Burke–Ernzerhof (PBE) scheme of the generalized gradient approximation (GGA).<sup>41</sup> PseudoDojo<sup>42</sup> was used for the LCAO calculation to describe the interaction between ion cores and valence electrons. Valence orbitals were



considered with a kinetic energy cut-off of 90 Ry and a  $3 \times 3 \times 1$  Monkhorst–Pack  $k$ -point mesh was used. We used a vacuum spacing of 16–20 Å perpendicular to the basal planes to avoid image–image interactions across the periodic boundary. The geometries were optimized using a conjugate gradient algorithm where the atoms were allowed to relax until the residual force and energies were smaller than  $0.025 \text{ eV \AA}^{-1}$  and  $1 \times 10^{-4} \text{ eV}$ , respectively. The Brillouin zone was integrated with Blöchl corrections using a broadening width of  $0.005 \text{ eV}$ .<sup>43,44</sup> The van der Waals corrections were included by Grimme's DFT-D3 method,<sup>45,46</sup> in order to include the dispersion corrections.

Optical calculations were evaluated based on the random phase approximation (RPA).<sup>47</sup> The optical properties of the interfaces in this study are discussed by the two components of the dielectric function  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  related to different polarizations in the electric field. The imaginary part  $\varepsilon_2(\omega)$  of the dielectric coefficient can be obtained from the direct interband transitions through Fermi's golden rule as in eqn (3)<sup>48–50</sup>

$$\varepsilon_2(\omega) = \frac{4\pi^2}{\Omega\omega^2} \sum_{i \in \text{HOMO}} \sum_{j \in \text{LUMO}} \sum_k W_k |\rho_{ij}|^2 \delta(\varepsilon_{kj} - \varepsilon_{ki} - h\omega) \quad (3)$$

where the HOMO, LUMO,  $\omega$ ,  $\Omega$ ,  $W_k$ , and  $\rho_{ij}$  denote the valence band, conduction band, photon frequency, volume of the lattice, weight of the  $k$ -point, and elements of the dipole transition matrix, respectively.

Moreover, the real part ( $\varepsilon_1(\omega)$ ) of the dielectric constant can be obtained with the following eqn (4)

$$\varepsilon_1(\omega) = 1 + \frac{1}{\pi} P \int_0^\infty d\bar{\omega} \frac{\bar{\omega} \varepsilon_2(\bar{\omega})}{\bar{\omega}^2 - \omega^2} \quad (4)$$

We discussed the absorption coefficient ( $\alpha_x(\omega)$ ) which is ascribed by eqn (5):

$$\alpha_x(\omega) = \frac{\omega \text{Im}[\varepsilon_x(\omega)]}{cn_x(\omega)} \quad (5)$$

where  $c$  denotes the speed of light, and  $n_x(\omega)$  refers to the refractive index.

## Conclusions

In this work, we used first-principles calculations to predict the adsorption of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) structures on different substrates consisting of sapphire(*c*-cut), sapphire(*r*-cut), SrTiO<sub>3</sub>(001), SrTiO<sub>3</sub>(111), SrNbO<sub>3</sub>(001), SrNbO<sub>3</sub>(111), LaAlO<sub>3</sub>(*c*-cut), and LaAlO<sub>3</sub>(*r*-cut). Using cell optimization and total energy calculations, we compare the relative surface energy, adsorption energy, optical adsorption and dielectric constants of the interfaces. The surface energy calculations show that there is a considerable difference in relaxation of the slabs comparing the VO<sub>2</sub>(M) and VO<sub>2</sub>(B) polymorphs. A comparison between surfaces revealed that the surface energies of fully relaxed SrTiO<sub>3</sub>(111) in VO<sub>2</sub>(M) and SrNbO<sub>3</sub>(001) in VO<sub>2</sub>(B) have considerably larger surface energy than other slabs with  $31.8 \text{ eV nm}^{-2}$  and  $21.15 \text{ eV nm}^{-2}$ , respectively. The adsorption energy calculations revealed that the interface of the VO<sub>2</sub>(M) polymorph is more favorable on

SrTiO<sub>3</sub>(001) with an adsorption energy of 2.83 eV, while VO<sub>2</sub>(B) has stability on SrTiO<sub>3</sub>(111) and sapphire(*c*-cut) with corresponding adsorption energy values of 0.91 and 1.11 eV, respectively. The optical absorption properties of the most stable (VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111)) and less stable (VO<sub>2</sub>(M)@sapphire(*c*-cut) and VO<sub>2</sub>(B)@sapphire(*c*-cut)) interfaces have been assessed. Both interfaces of VO<sub>2</sub>(M)@SrTiO<sub>3</sub>(001) and VO<sub>2</sub>(B)@SrTiO<sub>3</sub>(111) showed the adsorption in visible light, while VO<sub>2</sub>(M)@sapphire(*c*-cut) and VO<sub>2</sub>(B)@sapphire(*c*-cut) indicated the main first adsorption peak in the infrared region of the electromagnetic light. Differences in the stability and optical behaviours of VO<sub>2</sub>(M) and VO<sub>2</sub>(B) interfaces on different substrates suggest a path for the creation of new symmetry-mismatched heterostructures applicable in VO<sub>2</sub>-based electronics and optoelectronic devices.

## Author contributions

Conceptualization: E. M., E. L. and P. S.; methodology: E. M. and E. L.; validation: E. M., E. L., P. S., L. P., and D. M.; investigation: E. M.; data curation: E. M.; writing – original draft preparation: E. M.; writing – review and editing: E. M., E. L., E. P., P. S., L. P., and D. M.; visualization: E. M.; supervision: P. S.; project administration: E. M., E. L., E. P., P. S., L. P. and D. M. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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