Fermi level density of states modulation without charge transfer in nickelate superlattices

Myung Joon Han\textsuperscript{1,2,3} and Michel van Veenendaal\textsuperscript{2,3}

\textsuperscript{1} Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
\textsuperscript{2} Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
\textsuperscript{3} Department of Physics, Northern Illinois University, De Kalb, IL 60115, USA

E-mail: mj.han@kaist.ac.kr

Received 22 November 2013, revised 31 December 2013
Accepted for publication 15 January 2014
Published 18 March 2014

Abstract

By using first-principles density functional theory calculations for (LaNiO\textsubscript{3})\textsubscript{m}/(SrTiO\textsubscript{3})\textsubscript{n} superlattices, we report a systematic electronic response to the interface geometry. It is found that the density of states at the Fermi level of metallic nickelate layers is significantly reduced without charge transfer in the vicinity of the interface to the insulating SrTiO\textsubscript{3}. This type of electronic state redistribution is clearly distinctive from other interface phenomena such as charge and orbital reconstruction. Our result sheds new light on the understanding of the nickelates and other transition-metal oxide heterostructures.

Keywords: transition-metal oxide interface, electronic structure, density functional theory

1. Introduction

Recent advances in layer-by-layer growth techniques for transition-metal oxide (TMO) heterostructures have created considerable research interest [1, 2]. In these artificially structured interfaces, many exotic material characteristics have been reported which are strikingly different from the bulk properties and characteristics of a typical semiconducting interface (non-TMO interface) [1, 2]. For example, early studies of Ti-based superlattices such as LaTiO\textsubscript{3}/SrTiO\textsubscript{3} (LTO/STO) and SrTiO\textsubscript{3}/LaAlO\textsubscript{3} (STO/LAO) have revealed that heterostructuring induces unique electronic processes in TMOs that can dramatically change the macroscopic material properties [3–6]. In these cases, it is widely believed that valence charge reconstruction and polar discontinuity can drive the interfaces to be metallic even if the two mother materials are good insulators. The orbital degrees of freedom are also found to be reconstructed at the interface between manganites and cuprates [7]. Other examples of emergent material properties caused by the heterostructure geometry include superconductivity [8] and magnetism [9–11]. These new findings raise the important question as to how the heterostructuring of TMO materials affects the density of states (DOS) close to the Fermi level and the related low-energy properties.

In this study, we report another type of electronic response to the interface geometry, namely, Fermi level DOS modulation caused by state redistribution without a valence change. Although this phenomenon exhibits similarities to charge and orbital reconstruction, it displays distinctive characteristics. We found that the Fermi level DOS is strongly modulated as a function of the location of nickel atoms relative to the interface. Our first-principles calculations of LaNiO\textsubscript{3} (LNO)/STO clearly demonstrate that this novel electronic modulation around the Fermi level is intrinsic to the structure itself, i.e., the heterostructuring of nickelates, and does not originate from other effects such as charge transfer, oxidation and valence change. Further analysis indicates that this kind of behavior can be a common feature of nickelate systems sandwiched by any wide-gap material. Our result sheds new light on the understanding of TMO interface phenomena.

It should be noted that (LNO)\textsubscript{m}/(STO)\textsubscript{n} is distinctive from widely studied systems such as LNO/LAO and LNO...
film [12–19] due to the possibility that Ti can have active d electrons around the Fermi level. Charge transfer can in principle take place between Ti and Ni. As an example, it would be instructive to compare LNO/STO to the LNO/LTO superlattice, in which the Ti can clearly have an electron in its d orbitals, and there may be the electron transfer from Ti to Ni, leading to the configuration of Ti as d^{0+δ} (or d^{1−δ} depending on the amount of charge transfer) and Ni as d^{8−δ} (or d^{7+δ}) [20]. This kind of charge transfer is known to play an important role in determining the magnetic properties of LNO/LaMnO$_3$ (LMO) [21–24]. However, in the case of LNO/STO, it is not clear if such an electron transfer would take place, especially for the case of m = n = 1. Note that (LNO)$_1$/STO$_1$ can also be identified as (SrNiO$_3$)$_1$/LTO$_1$, and this alternative specification of the system implies that Ti has a d$^1$ (LTO-like) configuration instead of d$^0$ (STO-like). As we will show below, this possibility is not realized and Ti remains d$^0$ even in the m = n = 1 case, while Ni is d$^1$ (we drop the indication of the ligand hole for simplicity). From this interesting finding, important questions arise: if there is no charge transfer between the transition-metal (TM) ions, what happens at the interface? In other words, under the condition that no charge transfer is allowed, what kind of response can be made by the metallic material, LNO, in the vicinity of the interface to the insulating STO? Would the interface Ni exhibit the same characteristics as the inner layer Ni? If not, what possibilities exist for Ni in this superlattice geometry? This is a well-defined open question that has never been addressed clearly before.

Our calculations show that the Ni-d states are actually adjusted at the interface in a systematic way such that its DOS is redistributed while keeping the same total number of electrons. This implies that the interface Ni, closer to the insulating STO, becomes more insulator-like in the sense that its Fermi level DOS is reduced while the inner layer Ni becomes more metal-like in the sense that there is a higher DOS at the Fermi level.

2. Computation details

For band structure calculations, we employed a norm-conserving pseudopotential with partial core correction and a linear combination of localized pseudo-atomic orbitals (LCPAO) as a basis set [25]. We adopted the local density approximation (LDA) for the exchange–correlation energy functional as parametrized by Perdew and Zunger [26], using an energy cutoff of 400 Ryd and k-grid of 12 × 12 × 6 per unit volume. It is noted that bulk LNO is a paramagnetic metal down to low temperatures and that there have been no reports yet on the magnetic order in LNO/STO, even though a theoretical calculation discussed other possibilities [27]. Importantly, a recent standing-wave x-ray photoemission spectroscopy (SWXPS) measurement also assumed the paramagnetic phase [28], which will serve as the main experimental reference for our calculation. Therefore, a conventional LDA can be the best choice not only because it has been widely used in previous studies to describe paramagnetic LNO, but also because the LDA + U type of calculation has to assume a long-range ordered magnetic phase.

3. Result

3.1. Classification of Ni types and modulation of the Fermi level DOS

In LNO/STO, four different Ni sites exist considering their local environment. Nickel can be located either between two La$^{3+}$O$^{2−}$ layers or between the La$^{3+}$O$^{2−}$ and Sr$^{2+}$O$^{2−}$ layers. Furthermore, its neighboring TM can be either titanium or nickel (see the inset of figure 1). If a nickel ion is located between two La$^{3+}$O$^{2−}$ layers and its two neighboring TM sites are both Ni, it is bulk-like. At the interface, there are three different local structures, denoted as I1, I2, and I3 in the inset of figure 1. As the electronic structure of Ni can be affected by both of these two factors (the neighboring TM ions and the ionic potentials caused by A-site cations), it is important to understand these effects on Ni electronic structures. We will discuss this point below in further detail.

Recent depth-resolved SWXPS studies [28] show that the near-Fermi-level nickel states in (LNO)$_d$/STO$_3$ are significantly suppressed at the interface. A detailed analysis of the angular behavior of the SWXPS spectra indicates reduction

![Figure 1. The calculated Fermi level DOS for various (m, n) combinations of superlattices. The z-axis positions of Ni ions are renormalized so that the first NiO$_2$ layer is located at z = 0 and the last is located at z = 1. (Inset) Four different types of Ni sites existing in the (LNO)$_m$/STO$_n$ superlattice. Dark gray and light blue circles represent Ni and Ti, respectively. Solid and dotted vertical bars between transition metals represent SrO and LaO layers, respectively. Nickel of type I1 is located between the TiO$_2$–SrO and LaO–TiO$_2$ layers, type I2 between TiO$_2$–SrO and LaO–NiO$_2$, and type I3 between NiO$_2$–LaO and LaO–TiO$_2$. Nickel of type B is in the bulk-like arrangement located between NiO$_2$–LaO and LaO–NiO$_2$.](image-url)
of the electronic states at the two outer LNO layers adjacent to the STO layers (type I2 and I3 nickel in our definition), but not in the inner layers (bulk-like nickel). It was speculated in [28] that the variation in the Fermi level DOS could be due to the different oxidation of Ni ions; however, no further experimental evidence or explanation was provided.

3.2. DOS redistribution without charge transfer

We note that a clear understanding of this DOS modulation is of significant importance. If there is a charge transfer between TM ions, it is quite natural to expect that the value of the DOS changes at the Fermi level. Interestingly, however, our calculation shows that such a charge transfer and oxidation process are not responsible for this DOS modulation. We performed calculations for (LNO)$_m$/STO$_n$ with $(m, n) = (1, 1), (2, 2), (3, 3), (4, 1), (4, 3)$ and $(5, 2)$, and found that the number of $e_g$ electrons is 2.36–2.39, regardless of the type of nickel. From the point of view that all the nickel remains in the same charge status, the observed DOS modulation is unexpected and hard to explain using the ‘electronic reconstruction’ processes that were suggested before.

The fact that there is no valence change or further oxidation of Ni may be most dramatically seen in the $m = n = 1$ case, for which the alternative characterization of the superlattice as (SNO)$_1$/LTO$_1$ is also possible if the charge transfer (from Ni to Ti) were really to happen. Since Ti has the d$^0$ configuration in LTO while it is d$^1$ in STO, and the result can be clearly seen in the Ti states. The calculated Ti-d DOS in figure 2(b) shows that all the Ti-d states are empty. Therefore one can identify the system as (LNO)$_1$/STO$_1$ and there is no charge transfer between Ni and Ti even in the $m = n = 1$ case.

The effect of asymmetry in the A-site cation potential (i.e., Sr$^{2+}$ versus La$^{3+}$) causes no significant change in the electronic structure. This effect can be studied by examining the $(3, 3)$ heterostructure, for example, that contains both type I2 and I3 nickel ions (compare the dotted (blue) and dashed (green) lines in figure 3(b)). Since the two nickel ions only differ due to the A-site cations, the different electronic structure reflects the effect due to the A-site asymmetry. Figure 3(b) shows that the DOS change is small. In addition, for other $(m, n)$ structures, the projected DOS for type I2 and I3 nickel is always similar (seen in figure 4(b) for the case of $(5, 2)$) or upon comparison of the Fermi level DOS value at $z = 0$ and $z = 1$ in figure 1). Therefore, valence reconstruction is not relevant in this nickelate system, presumably due to the strong covalency.

Now, considering that the nickel valence states are all the same regardless of their position and the effect of the cation potential, it is quite surprising that the Fermi level DOS varies significantly. The calculated value of this quantity is summarized in figure 1, where the DOS values at the Fermi

---

**Figure 2.** (a) Projected Ni-eg DOS in the $(1, 1)$ superlattice. Red (solid) and blue (dashed) lines represent the $d_{x^2−y^2}$ and $d_{z^2}$ states, respectively. (b) Projected Ti-t$_{2g}$ DOS in the $(1, 1)$ superlattice. Blue (dashed) and red (solid) lines represent the $d_{xy}$ and $d_{z^2}$ states, respectively. Vertical dotted lines indicate the position of the Fermi level.

**Figure 3.** (a) Tight-binding calculation results for the weight of the central atom $|⟨E_i|E⟩|^2$ in the energy eigenfunction $|E⟩$. The length of the chain corresponds to the thickness of the LNO layer—that is, the $m$ in (LNO)$_m$/STO$_n$. The central position is given by $i_c = m/2$ and $(m + 1)/2$ for even and odd $m$, respectively. The energy unit used is the hopping parameter $t$. (b) Projected $d_{x^2−y^2}$ DOS for the $(3, 3)$ case. As expected, the bonding, nonbonding and antibonding characteristics are most clearly seen in the case of $(3, 3)$. Type I2, I3 and B states are represented by dotted (blue), dashed (green) and solid (red) lines, respectively. The Fermi level is set to be zero. (c) The projected $d_{x^2−y^2}$ DOS for bulk-type Ni in the $(3, 3), (4, 1),$ and $(5, 2)$ structures. For comparison, type I2 in $(2, 2)$ is also shown (red). The Fermi level is set to be zero. The asterisks indicate the peak positions.
Figure 4. (a) Schematic illustration of DOS reduction at the Fermi level as a function of layer position relative to the interface. The reduced DOS is transferred to the lower energy region. (b) Projected $d_{3z^2-r^2}$ DOS of two interface layer nickels (blue and green) and the inner layer nickel (red) in the $(5, 2)$ superlattice. The arrow indicates the amount of DOS reduction. (c) Integrated $d_{3z^2-r^2}$ DOS for the $(5, 2)$ case. The interface and innermost layer state are depicted in green and blue, respectively.

level (projected onto the different nickel sites) are plotted. It is clear that the interfacial nickel ions (see figure 1, where the $z$-position is normalized so that types I1, I2 and I3 are located either at $z = 0$ or at $z = 1$) always have a notably smaller Fermi level DOS than bulk-like nickel ($0 < z < 1$ in figure 1). The difference becomes even more pronounced as the number of Ni layers increases from $m = 3$ to $m = 5$. For $m = 5$, the Fermi level DOS for the innermost layer Ni ions is larger by a factor $\sim 2$ when compared with that of the interfacial layer. Since there is no charge transfer and no valence change, but a strong DOS modulation at the Fermi level, the DOS should be redistributed in such a way that the total number of electrons is kept the same. Further analysis shows that the DOS is actually redistributed in a systematic way such that the Fermi level DOS gradually decreases as the nickelate layer gets closer to the interface. In order to keep the charge valence unchanged, this weight is transferred to the lower energy region, as schematically shown in figure 4(a). It is interesting to note that the metallic LNO layers become more insulator-like when they come closer to the insulating STO, while keeping the same valence charge; that is, there is a lower number of states at the Fermi level. On the other hand, the inner LNO layers, far away from STO, become more
metallic in the sense that they have a greater DOS at the Fermi level.

Figure 4(b) shows that the reduction of the DOS is quite significant. As seen in figure 4(b), the $d_{z^2-r^2}$ states of the innermost (B; bulk-like) nickel is much greater than the two interface nickels (I2 and I3). The arrow indicates the DOS reduction at the Fermi level. The reduced states are transferred to the lower energy regions in the case of interface nickel sites, as clearly shown in the integrated DOS plot (figure 4(c)).

3.3. Mechanism of redistribution

To understand the mechanism behind the DOS modulation or redistribution process, a relatively simple picture can be considered based on the interactions between the molecule-like quantum states formed by the heterostructure geometry. As a starting point, let us consider the $m = n = 1$ case. As seen in figure 2(a), the bandwidth of the $d_{z^2-r^2}$ state is markedly narrower than that of the $d_{z^2-r^2}$ state, which is a result of limited hybridization along the $z$ direction by the presence of STO layers. From this characteristic of the $d_{z^2-r^2}$ state, one can treat it as a remnant of the molecular-orbital character arising from a chain of $md_{z^2-r^2}$ orbitals along the $z$ direction. These molecular-orbital-like features are further confirmed by the DOS shape of the (3, 3) case; figure 3(b) clearly shows features related to the bonding, antibonding and nonbonding states of the $m = 3$ chain. It is noted that the DOS of the bulk-type nickel (solid-red line) is strongest in the bonding and antibonding features at $\sim 0$ and $\sim 2.2$ eV.

This point is further supported by our tight-binding analysis, which captures the essence of the features found in the first-principles results. Assuming that the system can be approximately treated as a linear chain of $m$-molecular orbitals, we constructed a tight-binding model Hamiltonian corresponding to $N$ atoms, $H = \sum_{i=1}^{N} t c_i^\dagger c_j$, where $c_i^\dagger$ creates an electron at the $i$th site in the $z$ direction. The weight of the central (bulk-like) atom $|\langle c_i | E \rangle|^2$ is plotted in figure 3(a) as a function of energy $E$ (in units of $t$). As the chain length, $m$, increases from $m = 1$ to 3 and 5, the states interact with each other and spread out over a wide energy range. For $m = 3$, the two-peak feature of bonding and antibonding is most clearly seen, which is consistent with the results of our first-principles calculation in figure 3(b). Another important point in this analysis is that the bonding-peak position gradually shifts toward the lower energy region as $m$ increases (marked by the asterisks in figure 3(a)). Figure 3(c) shows that this characteristic behavior of the lower energy region of the $d_{z^2-r^2}$ states is also found in the first-principles calculations: as the number of layers increases, the peak position (marked by asterisks in figure 3(c)) shifts towards the lower energy region. It is the electronic origin that leads to a strong modulation in the number of states at the chemical potential shown in figure 1.

4. Discussion

The Fermi level DOS modulation has features distinct from other interface reconstructions. In general, electronic [4] and orbital [7] reconstructions depend on the relative on-site energies of interfacial ions, leading to a redistribution of charge between different sites and orbitals. In contrast, Fermi level DOS modulations involve a strong redistribution of states within the same sites and the same orbitals due to the presence of the interface. Since the low-energy properties are mainly determined by the states close to the chemical potential, strong position-dependent electronic properties can be expected and macroscopic properties (e.g., resistivity) should be sensitive to this strong modulation. Direct observation of this kind of electronic response is difficult as the charge valence of the interface remains unchanged, and only the near-Fermi-level DOS should be measured. However, we note that SWXPS can be used for the verification of our results and that the recent experiment by Kaiser et al for $(m = 4, n = 3)$ compares well with our conclusion [28].

Our analysis can be applied to other superlattice structures with LNO sandwiched by any wide-gap insulator in which the hybridization is strongly blocked only along the $z$ direction. Therefore, the same type of DOS modulation should be found in related heterostructures unless other types of response occur beforehand. To verify this point, we calculated the Fermi level DOS for $(LNO)^m/(LAO)^n$ with $(m, n) = (3, 3), (4, 1), (5, 2)$, and found that the same modulation occurs in this different systems. It is noteworthy that our tight-binding analysis based on the molecular-orbital chain model is better applied to the case of LNO/LAO. We expect DOS modulation to be a universal feature in nickelate superlattices and possibly also in other interfaces between metals and insulators.

Fermi level DOS reduction at the interfaces can provide an interesting new picture for the nickelate superlattices. We note that the DOS reduction at the interface is observed for all compositions of $(m \geq 3, n)$, while for $m \leq 2$, only the interface nickel ions exist and there are no bulk-like ones. Interestingly, several experiments on nickelate superlattices independently report that the MIT occurs at $m \approx 3$. The same critical thickness has been commonly observed in LNO/STO [29], LNO/LAO [30], LNO/SrMnO$_3$ [31], and LNO/LMO [22]. It is therefore tempting to relate the metallic and insulating phase to the bulk-like (B) and interface-like (I1, I2, I3) nickel layers, respectively, as the bulk-like nickel has more states at the Fermi level and starts to appear at $m = 3$. Further, a recent experiment by Boris and co-workers reported that this MIT is accompanied by a paramagnetic to magnetic transition [30]. We note that, in Kondo-type screening, the screening strength is governed by the Fermi level DOS, as is clear from the Kondo temperature scale, $T_K \sim e^{-1/\rho_0 K}$, where $\rho_0$ refers to the Fermi level DOS. Therefore, it may be interesting to regard nickelate superlattices as a kind of Kondo lattice system where the enhanced Fermi level DOS is responsible for the metallic conduction and simultaneously for screening of the local magnetic moments.

In the real experimental situations, there may be other possibilities for the nickelate layers to adjust to the heterostructure geometry. For example, distortion of the oxygen octahedra and charge disproportionation can be important in the thin film LNO [32, 16, 27]. In this system of LNO/STO, a similar type of ionic displacement can also be realized [33, 27], although this
possibility cannot be examined within our unit cell setup. Our calculations show that even without atomic distortion and/or charge transfer, the system has an electronic way of responding to the interface geometry.

Since LDA has limitations in describing electron correlations, the effect of correlations in Ni-3d on the DOS modulation could be a topic for future study. Here we note the previous dynamical mean-field study for the LNO/LAO-type superlattice [17], which indicates that the electronic DOS is not much affected by increasing \( U \) in as far as the double-counting energy is properly dealt with. Also considering the good agreement with the SWXPS result, our conclusion is well justified, at least for the paramagnetic and metallic region of phase space.

5. Summary

We report modulation of the Fermi level DOS across the LNO layers in LNO/STO superlattices. This modulation is caused by heterostructuring itself, with no valence change or oxidation, and is in good agreement with a recent SWXPS experiment. It is related to—but clearly distinct from—other interface phenomena such as orbital and valence reconstruction. Our analysis demonstrates that this electronic response to the hetero-interface structure originates from the novel process of quantum state formation and interactions between them. It can be related to MIT in related systems, providing a new theoretical aspect to research into complex TMOs.

Acknowledgments

This work was supported by the US Department of Energy (DOE), DE-FG02-03ER46097, and NIU’s Institute for Nanoscience, Engineering, and Technology. The work at the Argonne National Laboratory was supported by the US DOE, Office of Science, Office of Basic Energy Sciences under contract no. DE-AC02-06CH11357. Computational resources were provided by the National Institute of Supercomputing and Networking/Korea Institute of Science and Technology Information with supercomputing resources including technical support (grant no. KSC-2013-C2-005).

References

[1] Mannhart J, Blank D H A, Hwang H Y, Millis A J and Triscone J M 2008 Bull. Mater. Res. Soc. 33 1027
[2] Hwang H Y, Iwasa Y, Kawasaki M, Keimer B, Nagaosa N and Tokura Y 2012 Nature Mater. 11 103
[3] Ohtomo A, Muller D A, Grazul J L and Hwang H Y 2002 Nature 419 378
[4] Okamoto S and Millis A J 2004 Nature 428 630
[5] Ohtomo A and Hwang H Y 2004 Nature 427 423
[6] Nakagawa N, Hwang H Y and Muller D A 2006 Nature Mater. 5 204
[7] Chakhalian J, Freeland J W, Habermeyer H-U, Cristiani G, Khaliullin G, van Veenendaal M and Keimer B 2007 Science 318 1114
[8] Reyren N et al 2007 Science 317 1196
[9] Brinkman A, Huijbens M, van Zalk M, Huijbens J, Zeitler U, Maan J C, van der Wiel W G, Rijnders G, Blank D H A and Hilgenkamp H 2007 Nature Mater. 6 493
[10] Li L, Richter C, Mannhart J and Ashoori R C 2011 Nature Phys. 7 762
[11] Bert J A, Kalisky B, Bell C, Kim M, Hikita Y, Hwang H Y and Moler K A 2011 Nature Phys. 7 767
[12] Son J, Moetakef P, LeBeau J M, Ouellette D, Balents L, Allen S J and Stemmer S 2010 Appl. Phys. Lett. 96 062114
[13] Hansmann P, Toschi A, Yang X, Andersen O K and Held K 2010 Phys. Rev. B 82 235123
[14] Han M J, Marianetti C A and Millis A J 2010 Phys. Rev. B 82 134408
[15] Han M J and van Veenendaal M 2011 Phys. Rev. B 84 125137
[16] Liu J, Okamoto S, van Veenendaal M, Kareev M, Gray B, Ryan P, Freeland J W and Chakhalian J 2011 Phys. Rev. B 83 161102(R)
[17] Han M J, Wang X, Marianetti C A and Millis A J 2011 Phys. Rev. Lett. 107 206804
[18] Han M J and van Veenendaal M 2012 Phys. Rev. B 85 195102
[19] Sakai E, Tamamitsu M, Yoshimatsu K, Okamoto S, Horiba K, Oshima M and Kumigashira H 2013 Phys. Rev. B 87 075132
[20] Chen H, Marianetti C A and Millis A J 2013 Phys. Rev. Lett. 111 116403
[21] Gibert M, Zubko P, Schweritzel R, Íñiguez J and Triscone J-M 2012 Nature Mater. 11 195
[22] Hoffman J, Tung I C, Nelson-Cheeseman B B, Liu M, Freeland J W and Bhattacharya A 2013 Phys. Rev. B 88 144411
[23] Dong S and Dagotto E 2013 Phys. Rev. B 87 195116
[24] Lee A T and Han M J 2013 Phys. Rev. B 88 035126
[25] Ozaki T et al Open source package for Material eXplorer (http://openmx-square.org)
[26] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048
[27] Ceperley D M and Alder B J 1980 Phys. Rev. Lett. 45 566
[28] Kaiser A M 2011 Phys. Rev. Lett. 107 116402
[29] Son J, LeBeau J M, Allen S J and Stemmer S 2010 Appl. Phys. Lett. 97 202109
[30] Boris A V et al 2011 Science 332 937
[31] May S J, Santos T S and Bhattacharya A 2009 Phys. Rev. B 79 115127
[32] Chakhalian J et al 2011 Phys. Rev. Lett. 107 116805
[33] Hwang J, Son J, Zhang J Y, Janotti A, Van de Walle C G and Stemmer S 2013 Phys. Rev. B 87 060101(R)