DOI: 10.1002/((please add manuscript number))
Article type: Communication

Oxy-nitride Multilayers as a Platform for Parallel Two-Dimensional Electron-Hole Gases: MgO/ScN(111)

*Antia S. Botana, Victor Pardo, and Warren E. Pickett**

Dr. Antia S. Botana and Prof. Warren E. Pickett

Department of Physics, University of California Davis, Davis, California 95616, USA

Email: wepickett@ucdavis.edu

Dr. Victor Pardo

Departamento de Fisica Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

Instituto de Investigacions Tecnoloxicas, Universidade de Santiago de Compostela, E-15782 Campus Sur s/n, Santiago de Compostela, Spain.

Keywords: heterostructures, oxides, nitrides, 2D-electron gas ((maximum five, not capitalized, plural, separated by commas, no full stop))

The unexpected magnetic and electronic phases appearing at the interface between two perovskite oxides have been studied extensively during the last decade.[1] The discovery of a two dimensional electron gas (2DEG) at the interface between $LaAlO_3$/ $SrTiO_3$(LAO/STO) by Ohtomo and Hwang[1] stimulated excitement for the design of similar heterostructures and their possible use in electronic devices.[2] The further realization that electronic reconstruction

could lead to a parallel, nanoscale 2DEG and 2DHG (2D hole gas) provided a more exotic vista,[1,3] including two band, two carrier magnetic or superconducting systems, as well as long sought excitonic condensates.[4] Unfortunately, at oxide interfaces the hole gas has never materialized. Due to the proclivity of holes to occupy O *2p* orbitals, it is always observed to be non-conducting, eliminating the many possibilities provided by a two, or many, 2DEGs and 2DHGs separated by only a nm or two.[5]

The difficulty in obtaining conducting *p*-type interfaces in oxides suggests using nitrides. Whereas *3d* transition metal monoxides include the strongly correlated (Mott) insulators, the corresponding mononitrides are usually conducting and even superconducting.[6] This tendency toward conductivity reflects a decreased electronegativity and more itinerant behavior suggesting the use of the N ion in heterostructures.

(001) layers of transition metal mononitrides (or monoxides) with rocksalt structure are charge neutral, thus being ineffective in providing the electron gases of interest here. This layer neutrality, and the challenges provided by localized O-*2p* states, invites innovative material design, especially because layer-by-layer growth provides the experimental capability of concerted theory plus experiment design of novel materials.

The simplest polar structure in mononitrides is provided by (111) orientation growth, where oppositely charged metal and anion-atom layers alternately stack along the [111] direction. MgO films with an atomically flat (111) surface have been obtained using layer-by-layer growth on different substrates. [7] The atomically flat surfaces obtained in MgO(111) films are promising to explore the possibility of polar interface engineering using simple metal monoxides and mononitrides with rocksalt structure.

Here, we explore the use of the narrow gap semiconductor ScN, [8] sandwiched between highly insulating MgO,[9] as a material to support bilayer electron+hole conducting gases and all the unusual phases that have been anticipated in such heterostructures. We have designed MgO/ScN(111) superlattices with varying ScN thickness containing two charge imbalanced

interfaces: one *n*-type and one *p*-type. First principles calculations show that beyond an ScN thickness threshold of five layers these interfaces host conducting electron+hole gases. Use of the N anion should promote robust two carrier 2D conduction compared to oxides, where holes are prone to localization.

As mentioned above, the (111) orientation of a rocksalt structure is polar and a crystal cut along (111) presents alternating layers of metal and oxygen/nitrogen ions forming a honeycomb-like structure in the *ab* plane (see **Figure 1**a and b). In the ScN side of the multilayer, there are N and Sc planes with formal charges 3- and 3+ respectively; in the MgO side, Mg and O layers with formal charges 2+ and 2- as shown in Figure 1c and 1d. When growing periodically arranged multilayers two charge imbalanced (polar) interfaces arise: the so-called interface A (IFA, n-type) (2-/3+) and interface B (IFB, *p*-type) (3-/2+).

Electronic structure of ScN/MgO multilayers. The polar nature of these multilayered systems will give rise to an intrinsic electric field formed as indicated by the arrows in Figure 1c and d. Induced by the polar discontinuities, one expects a large electrostatic potential offset between the two interfaces causing a sharp potential gradient. This effect can be seen by tracking the energy of the layer-by-layer core levels shown in Figure 1 for multilayers with different ScN thickness. A potential difference of 2 to 3 eV on each block of the multilayer develops (increasing with increasing thickness from three to six ScN blocks). This corresponds to a local electric field 1.1×10^{7} V/cm acting across the interface region, on the order of that obtained in LAO/STO heterostructures.[3,10] The layer-by-layer shifts in the core levels are about 1 eV in the thinner multilayer and are reduced when the ScN block is thicker. The superlattice periodicity forces the potential to return to zero after it has ramped up the ScN part.

As a consequence of this potential gradient due to interface polarity, there is an insulator-to-metal transition as the number of ScN layers is increased. For multilayers 3 ScN layers thick the gap (1.5 eV) is widened with respect to the value in the bulk (see the bulk band structure

in **Figure S1**), for 4 ScN layers the gap is reduced to 0.34 eV, and from 5 ScN layers onwards the band structures are metallic. Insulator-to-metal transitions with thickness have been observed in a number of oxide-based heterostructures in the literature, both polar and non-polar, including open-shell and closed-shell materials, such as multilayers of VO_2/TiO_2, [11] $SrVO_3/SrTiO_3$ [12] $LaVO_3/SrTiO_3$,[13] and the above mentioned $LaAlO_3/SrTiO_3$.[1]

The Sc and N contributions to the density of states for MgO/ScN multilayers three and six ScN layers thick are shown in **Figure 2**. The a and b panels show the insulator-to-metal transition as the number of ScN layers increases. The nearly rigid upward shift consistent with the above described potential gradient can be observed by focusing on the N-2p bands that move towards the Fermi level from IFA to IFB. For six layers of ScN, the layer-by-layer potential gradient is reduced significantly with respect to the thinner layers.

As explained above, for the thinner multilayers an insulating state is obtained (Figure 2a), a result of perpendicular confinement. The gap is formed between occupied N-*p* states and unoccupied Sc-*d* states, being widened with respect to that in the bulk, another effect attributed to confinement.

For the multilayers with a thicker ScN block (Figure 2b), N-*p* and Sc-*d* states appear at the Fermi level for both interfaces (and IF-1 layers) corresponding to a bilayer conducting state. This band overlap provides a bulk (multilayer) realization of the polar discontinuity scenario of electronic reconstruction, originally found for LAO overlayers on an STO substrate. In this process electrons are transferred from one interface of the unit cell to the other, thus reducing the internal field although a substantial gradient persists (of the order of 10^7 V/cm).

The conducting states arising at the interfaces have predominantly in-plane character giving further evidence of the 2D charge confinement: N $2p_x$, $2p_y$ hole-like states at IFB and Sc $3d_{x^2-y^2}$, $3d_{xy}$ electron-like states at IFA. The band structure and Fermi surface plots (shown in **Figures S2 and S3**, respectively) indicate that the nearly circular hole pocket is centered at Γ whereas the nearly circular electron pocket is centered at the hexagonal zone face *M*

point. The result is 2D bilayer conducting (hole+electron) states each confined to two atomic layers (IF and IF-1). This narrow confinement effect is an important ingredient in giving rise to a two-carrier-2D conduction in this type of heterostructures.

Using a transition metal nitride provides yet another opportunity. The superconductivity observed in many samples of STO/LAO may be simply the state observed in *n*-doped STO (confined somewhat to reflect a 2D superconducting behavior), or it might be due to an interfacial pairing mechanism. Mononitrides with a rocksalt structure (MN with M= Ti, Zr, V, and Nb) were among the first discovered superconductors with T_c's up to 16 K.[6] Also, electron-doped transition metal chloronitrides MNCl (M = Hf, Zr, Ti) are superconducting in the 15-26 K range,[14] putting them in the top six classes of high temperature superconductors. The observation of superconductivity at a transition metal nitride interface (as in this ScN/MgO system) is an exciting possibility, and if discovered would support that superconductivity observed at STO/LAO interfaces is intrinsically interfacial and 2D in origin.

Bilayer transport. Parallel electron-hole bilayers were pioneered in GaAs/AlGaAs heterostructures.[15] In LAO/STO (001) overlayers a parallel electron-hole conduction has been reported only when an STO capping layer is added to protect the uppermost 2DEG.[3] Transport and spectroscopic measurements combined with first principles calculations as well as scanning tunneling spectroscopy with variable temperature[3] support the realization of two spatially separated 2D conducting sheets: one electron-like and the other hole-like. The O-*2p* states of the capping layer enable hole doping at the electronically reconstructed interfaces. However, holes in O-*2p* states are characterized by a low mobility and tend to become localized.[5] For this reason, use of the N anion should promote more robust two carrier 2D conduction compared to oxides, and a capping layer may not be required. Hall measurements provide a standard probe of multiband transport.

To allow for an additional experimental test of the origin and nature of the conduction mechanism in these multilayers, we have calculated the temperature dependence of the thermopower *S(T)*. It is useful to review the expression for *S(T)* within Bloch-Boltzmann transport theory for a degenerate Fermi liquid. The Mott formula is

$$S(T) = \frac{\Pi^2 k_B^2 T}{3e} \frac{dlog\sigma(\varepsilon)}{d\varepsilon}\Big|_{\varepsilon=\mu(T)} (1)$$

$$\sigma(\varepsilon)\ \alpha\ N(\varepsilon)v^2(\varepsilon)\tau(\varepsilon)\ (2)$$

in terms of the energy-dependent conductivity $\sigma(\varepsilon)$ where k_B is the Boltzmann constant, *e* the charge of the carriers, $N(\varepsilon)$ the density of states, v the group velocity, and τ the scattering time. The energy dependence of τ depends on the scattering mechanism and is usually treated as unimportant on a fine energy scale, as we do here. For parabolic bands in 2D, $N(\varepsilon)$ is constant and the only energy dependence is from $v^2(\varepsilon)\ \alpha\ \varepsilon$, hence

$$S(T)\alpha\ \frac{\pi^2 k_B^2 T}{3e\mu(T)}\ (3)$$

where $\mu(T)$ is the chemical potential that is usually weakly *T*-dependent. When a two-carrier system develops, hole and electron contributions tend to compensate (for holes, $e \rightarrow -e$ in the expression for *S(T))* and may result in a small, almost temperature independent thermopower. The thermopower calculated from the more accurate Bloch-Boltzmann expressions,[16] which involves only Fermi surface quantities versus those from throughout the occupied bands (such as the carrier density), is shown in Figure 2c. Values of the thermoelectric power for electrons and holes are linear with T and virtually identical in size ($|dS/dT| = 0.11\ \mu V/K^2$). The thermopower including electron- and hole- like Fermi surfaces is weighted by the respective conductivities ($\sigma_{xx,i}$) in the following way $S_{xx} = \frac{\sum_i \sigma_{xx,i} S_{xx,i}}{\sum_i \sigma_{xx,i}}$ with *i* representing the band index. The two contributions compensate even though they do

not completely cancel due to the higher conductivity linked to the electron-like (Sc-*d* states) Fermi surface with respect to the hole-like one (N-*p* states). Figure 2d shows the density of states (DOS) of electron and hole bands separately, indicating a nearly flat, 2D-like electron DOS over a range of several k_BT (even at 400 K), while the hole DOS has a negative derivative.

The thermopower obtained in this ScN/MgO(111) multilayer is different than some behaviors discussed elsewhere. 2DEGs can be obtained in related interfaces but involving only one type of carrier.[17] Quantum confinement, which narrows (some) bands, may produce a thermopower enhancement.[18] Interestingly, ScN itself has been found to yield an anomalously large thermopower albeit at high doping level[19] suggested to result from localized impurity states close to the Fermi level.[20]

The calculated Hall coefficient for electron and hole-like bands gives $R_H = 0.11\times 10^{-7}\ m^3/C$, $R_e = -0.16\times 10^{-7}\ m^3/C$, both T-independent above 200 K, corresponding in a standard but simplistic interpretation to an effective carrier density (Hall number) $n_e = 3\times 10^{13}$ carriers/cm^2 and $n_h = 4\times 10^{13}$ carriers/cm^2 in the same range as in oxide-only interfaces but without implying additional electrons that may reside in localized states.[1, 3]

The classic textbook expression for a multi-carrier/multiband system demonstrates that electron and hole contributions are however not simply additive. The Bloch-Boltzmann semiclassical generalization demonstrates that for non-elliptical energy surfaces (as are two of the Fermi surfaces in this superlattice), the entwinement of electron and hole contributions is more involved. The general expression is

$$R^H = \frac{\sigma_{xyz}}{\sigma_{xx}\sigma_{yy}} \quad (4)$$

in terms of the Hall and conventional conductivity tensors. For two band (or two carrier) cases this becomes

$$R^H = \frac{\sigma^h_{xyz}+\sigma^e_{xyz}}{(\sigma^h_{xx}+\sigma^h_{xx})(\sigma^h_{yy}+\sigma^e_{yy})} \quad (5)$$

a result that is far from being an additive contribution from electrons and holes.

However, parallel superlattice 2DEGs of the type being discussed here constitute a new type of alternating metal-insulator multilayer: the electron and hole 2DEGs are distinct systems, but intimately so. As such, in evaluating *S(T)* and R^H above, the expressions from Bloch-Boltzmann theory (and the BoltzTraP code) have to be reconsidered. If in the definition

$$R^H_{xyz} = \frac{E_y}{j_x B_z} \quad (6)$$

the current j_x from both electron and hole 2DEGs is used, the result incorrectly incorporates quantities from two separate subsystems.

These superlattices correspond to alternately layered *n*- and *p*-type 2DEGs, each with its own Hall voltage given by its own current density, *i.e*. velocities and DOSs, and the common electric field. The contributions must be calculated separately, as we have done.

Discussion. Using first principles calculations, we have studied MgO/ScN(111) multilayers as a platform for the realization of a two dimensional, two carrier (electron+hole) gas. An insulator to metal transition takes place as the ScN thickness increases, with conducting states appearing at a critical thickness of five ScN layers. The two metallic layers are each confined to its own interface, with negligible overlap of the wavefunctions -- thus constituting a periodic array of alternating electron and hole 2DEGs. A central distinction of this system compared to previously studied interfacial systems is the use of the N anion for the hole bands

rather than the O anion. The less strongly bound *p* states of N should promote more robust two carrier 2D conduction compared to oxides, where holes are prone to localization.

We propose experimental tests for detecting this peculiar conducting state, i.e. thermopower and Hall effect measurements. Both should display considerable electron-hole compensation. Finally, we urge experimental studies of this and related nitride interfacial systems that they be checked down to sub-kelvin temperatures for superconductivity. The observation of superconductivity at a transition metal nitride interface is an exciting possibility, and if discovered would support that the superconductivity observed at STO/LAO interfaces is intrinsically interfacial and 2D in origin. Our study of ScN/MgO superlattices should lay the groundwork for new exploration, both experimental and theoretical, on nitride interfaces.

Computational Details

Our electronic structure calculations were performed within density functional theory[21] using the all-electron, full potential code WIEN2k[22] based on the augmented plane wave plus local orbitals (APW+lo) basis set.[23]

All calculations were well converged with respect to all the parameters used. In particular, we used $R_{MT}K_{max}$=7.0 (the product of the smallest of the atomic sphere radii R_{MT} and the plane wave cutoff parameter K_{max}) which determines the size of the basis set. The R_{MT} chosen are 1.95 a.u. for Sc, 1.73 a.u. for N, 1.79 a.u. for Mg and 1.69 a.u. for O. The calculations used a 43×43×5 *k*-mesh for the integrations over the Brillouin zone. For the structural relaxations we have used the Wu-Cohen (WC)[24] version of GGA that gives better lattice parameters for MgO than PBE.[25] The optimized lattice parameters derived within GGA-WC for MgO and ScN are 4.23 and 4.50 Å, respectively.

An accurate *ab initio* description requires a method able to reproduce the band gap of the individual components as well as their band alignment at the interface, both of which are

generally beyond the capabilities of the generalized gradient approximation (GGA) or local density approximation (LDA). To be able to reproduce the bulk gap of ScN, we have used the semilocal potential developed by Tran and Blaha based on a modification of the Becke-Johnson potential (TB-mBJ). This is a local approximation (local in the density and the kinetic energy density) to an atomic exact-exchange potential and a screening term + GGA correlation that allows the calculation of band gaps with an accuracy similar to the much more expensive GW or hybrid methods.[26] The TB-mBJ functional is a potential-only functional, i.e., there is no corresponding TB-mBJ exchange-correlation energy functional. In this respect it is applied as a self-energy correction, and one based on improved intra-atomic exchange processes. The bandstructure for bulk ScN obtained within TB-mBJ gives the correct band gap and is shown in the Supporting Information.

Based on the agreement with the experiments for ScN bulk, TB-mBJ was the scheme applied to the ScN/MgO (111) multilayers. We have modeled MgO/ScN(111) multilayers which are 2- to 7-ScN layers thick. A barrier of 4 MgO layers (about 1 nm thick) between ScN blocks has been used for all the calculations, checking that it is sufficient to guarantee the lack of interaction between ScN blocks. The multilayers are modeled with the in-plane lattice parameters constrained to those of MgO (fixed to the value 4.23 Å, obtained by optimizing the cell volume within WC-GGA).

For all the multilayers we performed calculations with fully relaxed atomic positions also optimizing the value of the *c*-lattice parameter (off-plane), i.e. allowing atomic displacements along the *c*-axis and thus relaxing the inter-plane distances for the structures with different number of ScN layers. The optimized values of the *c*-lattice parameter result in a slight increase from the value obtained by constructing the multilayers from the MgO bulk unit cell, of about 1 % to 2 % for multilayers two to seven ScN layers thick. This is expected, as the in-plane lattice parameter inside the ScN blocks is constrained to that of MgO, which is smaller (4.23 Å versus 4.50 Å for the cubic phase of ScN). The ScN block is subjected to compressive

strain due to the lattice mismatch (of about 5 %, an amount that can be sustained for several layers).

One of the main features in the calculated relaxed geometry is the presence of a considerable polar distortion in the ScN layers while there is negligible distortion on the MgO side. The atomic displacements are exclusively along the c-axis resulting on one shorter (2.07-2.09 Å) and one longer (2.15-2.19 Å) Sc-N or Sc-O bond.

The transport properties were calculated using a semiclassical solution based on Bloch-Boltzmann transport theory within the constant scattering time approximation by means of the BoltzTraP code,[27] which uses the energy eigenvalues calculated by the WIEN2K code. The constant scattering time approximation assumes that the energy dependence of the scattering time at a given temperature and doping level is negligible on the scale of k_B. In this case, denser *k*-meshes are required, in our case up to 118×118×14 to reach convergence.

Acknowledgments

V. P. thanks MINECO for project MAT2013-44673-R, the Xunta de Galicia through project EM2013/037, and Spanish Government for financial support through the Ramon y Cajal Program. W.E.P. acknowledges many conversations with R. Pentcheva on the theory and phenomenology of oxide interfaces and multilayers. A. S. B. was supported by the National Science Foundation Grant No. 1207622. W.E.P. was supported by Department of Energy Grant No. DE-FG02-04ER46111.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

References

[1] a) A. Ohtomo and H. Hwang, Nature 427, 423 (2004); b) S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider, and J. Mannhart, Science 313, 1942 (2006); c) A. D. Caviglia, S. Gariglio, C. Cancellieri, B. Sacepe, A. Fete, N. Reyren, M. Gabay, A. F. Morpurgo, and J. M. Triscone, Phys. Rev. Lett. 105, 236802 (2010); d) A. Brinkman, M. Huijben, M. van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. van der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, Nat. Mater. 6, 493 (2007); e) N. Reyren, S. Thiel, A. D. Caviglia, L. F. Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.S. Retschi, D. Jaccard, et al., Science 317, 1196 (2007).

[2] a) J. Mannhart and D. G. Schlom, Science 327, 1607 (2010); b) S. Park, D. H. Lee, J. Xu, B. Kim, S. W. Hong, U. Jeong, T. Xu, and T. P. Russell, Science 323, 030 (2009).

[3] a) R. Pentcheva, M. Huijben, K. Otte, W. E. Pickett, J. E. Kleibeuker, J. Huijben, H. Boschker, D. Kockmann, W. Siemons, G. Koster, et al., Phys. Rev. Lett. 104, 166804 (2010); b) M. Huijben, D. Kockmann, J. Huijben, J. E. Kleibeuker, A. van Houselt, G. Koster, D. H. A. Blank, H. Hilgenkamp, G. Rijnders, A. Brinkman, et al., Phys. Rev. B 86, 035140 (2012).

[4] a) A. Millis and D. G. Schlom. Phys Rev. B 82, 073101 (2010); b) J. Kunes arXiv:1505.01271; c) J. P. Eisenstein- and A. H. MacDonald- Nature 432, 691-694 (2004).

[5] H. Chen, A. Kolpak, and S. Ismail-Beigi, Phys. Rev. B 82, 085430 (2010).

[6] a) B. T. Matthias and J. K. Hulm, Phys. Rev. 87, 799 (1952); b) B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. 35, 1 (1963); c) F. Rivadulla, J. Fernández-Rossier, M. García-Hernández, M. A. López-Quintela, J. Rivas, and J. B. Goodenough, Phys Rev. B 76 205110 (2007).

[7] a) R. Arita, Y. Tanida, S. Entani, M. Kiguchi, K. Saiki, and H. Aoki, Phys. Rev. B 69, 235423 (2004); b) J. Goniakowski, C. Noguera, and L. Giordano, Phys. Rev. Lett. 93, 215702 (2004); c) J. Goniakowski, C. Noguera, and L. Giordano, Phys. Rev. Lett. 98, 205701 (2007); d) H. S. Craft, J. F. Ihlefeld, M. D. Losego, R. Collazo, Z. Sitar, and J.-P. Maria, Applied Physics Letters 88, 212906 (2006); e) T. L. Goodrich, J. Parisi, Z. Cai, and K. S. Ziemer, Applied Physics Letters 90, 042910 (2007); f) A. Posadas, F. J. Walker, C. H. Ahn, T. L. Goodrich, Z. Cai, and K. S. Ziemer, Applied Physics Letters 92, 233511 (2008); g) T. Susaki, S. Kumada, T. Katase, K. Matsuzaki, M. Miyakawa, and H. Hosono, Applied Physics Express 2, 091403 (2009); h) K. Matsuzaki, H. Hosono, and T. Susaki, Phys. Rev. B 82, 033408 (2010). i) K. Matsuzaki, H. Takagi, H. Hosono, and T. Susaki, Phys. Rev. B 84, 235448 (2011).

[8] a) A. R. Smith, H. A. H. AL-Brithen, D. C. Ingram, and D. Gall, Journal of Applied Physics 90, 1809 (2001); b) W. R. L. Lambrecht, Phys. Rev. B 62, 13538 (2000); c) H. Jiang, R. I. Gomez-Abal, P. Rinke, and M. Schefer, Phys. Rev. B 82, 045108 (2010).

[9] a) D. M. Roessler and W. C. Walker, Phys. Rev. 159, 733 (1967); b) K. Kenmochi, V. A. Dinh, K. Sato, A. Yanase, and H. Katayama-Yoshida, Journal of the Physical Society of Japan 73, 2952 (2004).

[10] D. F. Bogorin, C. W. Bark, H. W. Jang, C. Cen, C. M. Folkman, C. B. Eom, and J. Levy, Applied Physics Letters 97, 013102 (2010).

[11] V. Pardo and W. E. Pickett, Phys. Rev. B 81, 035111, 6 (2010).

[12] a) D. Kim, D.-W. Kim, B. Kang, T. Noh, D. Lee, K. B. Lee, and S. Lee, Solid State

Communications 114, 473 (2000); b) V. Pardo and W. E. Pickett, Phys. Rev. B 81, 245117 (2010); c) K. Yoshimatsu, T. Okabe, H. Kumigashira, S. Okamoto, S. Aizaki, A. Fujimori, and M. Oshima, Phys. Rev. Lett. 104, 147601 (2010).

[13] E. Assmann, P. Blaha, R. Laskowski, K. Held, S. Okamoto, and G. Sangiovanni, Phys. Rev. Lett. 110, 078701 (2013).

[14] Y. Kasahara, K. Kuroki, S. Yamanaka, and Y. Taguchi, Physica C, in press arxiv 1412.4447 (2015).

[15] J. A. Keogh, K. Das Gupta, H. E. Beere, D. A. Ritchie, and M. Pepper, Applied Physics Letters 87, 202104 (2005).

[16] P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B 37, 7482 (1988).

[17] H. Ohta, S. Kim, Y. Mune, T. Mizoguchi, K. Nomura, S. Ohta, T. Nomura, Y. Nakanishi, Y. Ikuhara, M. Hirano, et al., Nat. Mater 6, 129 (2007).

[18] a) L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B 47, 12727 (1993); b) J. O. Sofo and G. D. Mahan, Applied Physics Letters 65, 2690 (1994).

[19] a) S. Kerdsongpanya, N. Van Nong, N. Pryds, A. Ukauskait, J. Jensen, J. Birch, J. Lu, L. Hultman, G. Wingqvist, and P. Eklund, Applied Physics Letters 99, 232113 (2011); b) M. Zebarjadi, Z. Bian, R. Singh, A. Shakouri, R. Wortman, V. Rawat, and T. Sands, Journal of Electronic Materials 38, 960 (2009); c) P. V. Burmistrova, J. Maassen, T. Favaloro, B. Saha, S. Salamat, Y. Rui Koh, M. S. Lundstrom, A. Shakouri, and T. D. Sands, Journal of Applied Physics 113, 153704 (2013).

[20] S. Kerdsongpanya, B. Alling, and P. Eklund, Phys. Rev. B 86, 195140 (2012).

[21] a) P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); b) R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).

[22] K. Schwarz and P. Blaha, Computational Materials Science 28, 259 (2003).

[23] E. Sjostedt, L. Nordstrom, and D. Singh, Solid State Communications 114, 15 (2000).

[24] Z. Wu and R. E. Cohen, Phys. Rev. B 73, 235116 (2006).

[25] F. Tran, R. Laskowski, P. Blaha, and K. Schwarz, Phys. Rev. B 75, 115131 (2007).

[26] a) F. Tran and P. Blaha, Phys. Rev. Lett. 102, 226401 (2009); b) D. Koller, F. Tran, and P. Blaha, Phys. Rev. B 83,195134 (2011).

[27] G. K. Madsen and D. J. Singh, Computer Physics Communications 175, 67 (2006).

Figures

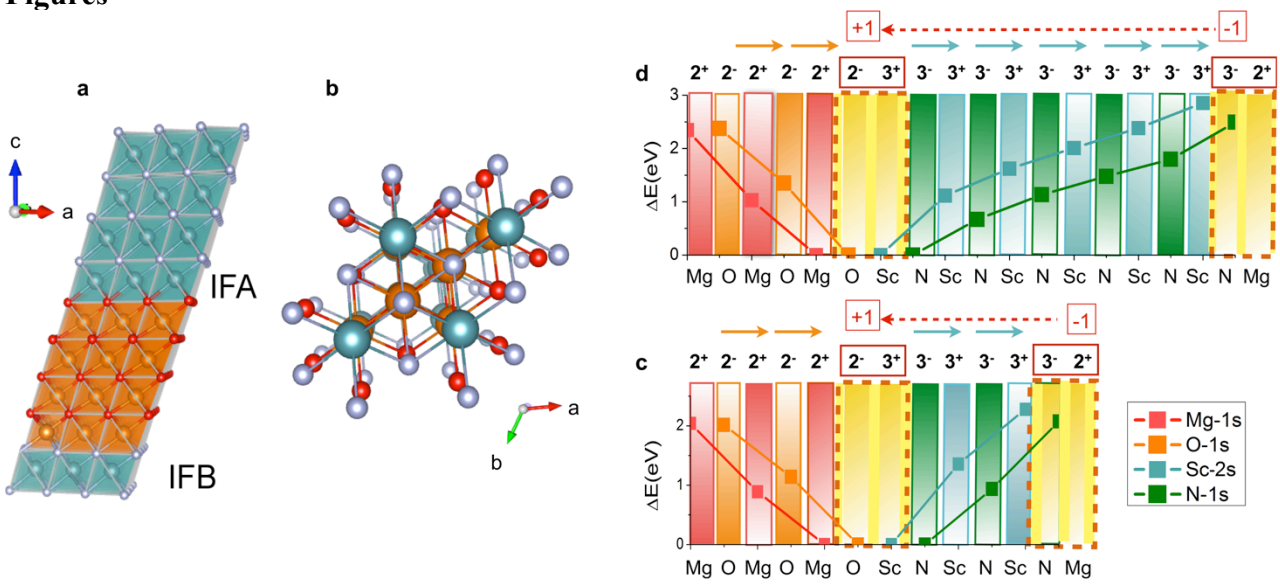

Figure 1. (a) Side view of the unit cell of ScN/MgO(111) multilayers five ScN layers thick with Sc atoms in blue, the N atoms in gray, Mg atoms in orange, and O atoms in red. IFA (O-Sc) and IFB (N-Mg) (b) Honeycomb-like structure of the multilayers in the ab plane. (c) and (d) show the layer-by-layer shifts for Mg-, N-, and O-1s (red, green and orange squares, respectively) and for Sc-2s (blue squares) core states for multilayers three (c) and six (d) ScN layers thick ΔE represents the value of the shift in eV). Yellow indicates the interface O-Sc (IFA) and N-Mg (IFB) regions. The zero is set at IFA. An electric field is formed from IFB to

IFA producing a potential build up across the multilayer of 2-3 eV. In the ScN side of the multilayer, there are N (in green) and Sc (in blue) planes with formal charges 3- and 3+. In the MgO side, Mg (in red) and O (in orange) layers have formal charges 2+ and 2-.

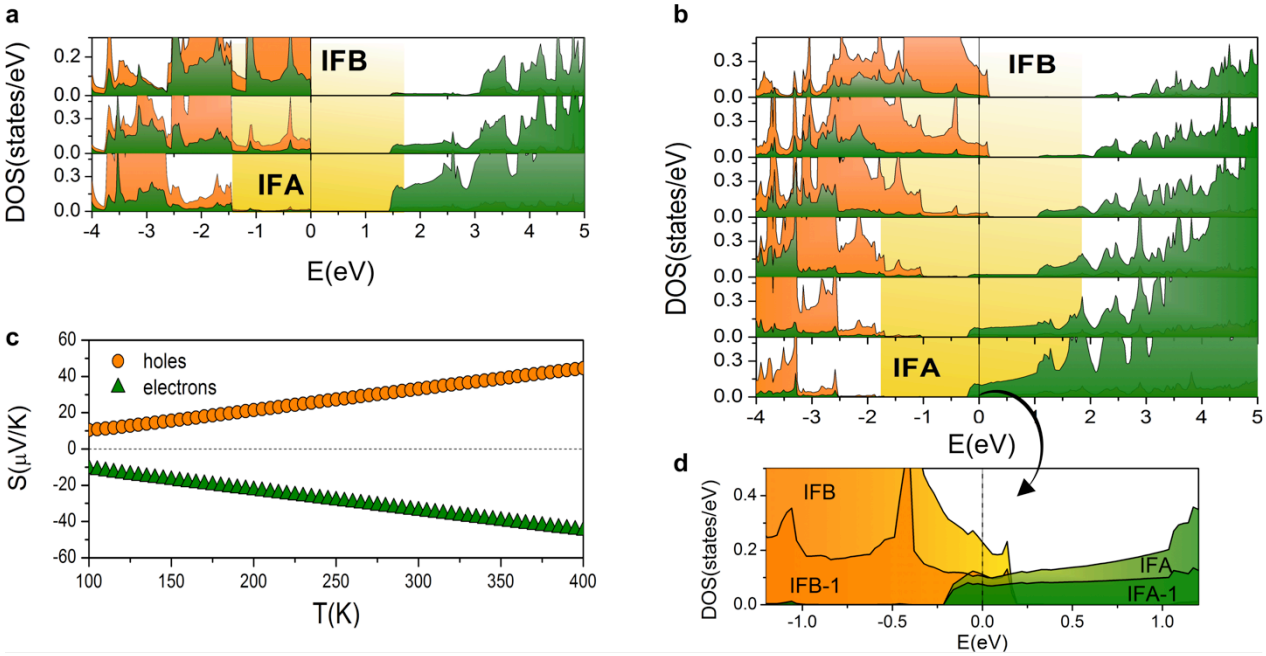

Figure 2. (a) and (b) Layer resolved density of states for Sc/N atoms across the ScN slab from IFB to IFA for ScN/MgO(111) multilayers three (a) and six (b) ScN-layers-thick. N-*p* states in orange, Sc-*d* states in green. The shift in the N-*p* and Sc-*d* (of almost 1 eV/layer) states as moving from IFA to IFB can be observed. (c) Temperature dependence of the in-plane thermopower for MgO/ScN multilayers six ScN layers thick for electrons and holes. The contributions to the net $S_{xx}(T)$ are discussed in the text. The calculations were done by summing over only the valence Fermi surfaces for the hole properties (orange), only over the conduction Fermi surfaces for the electron properties (green). (d) shows the density of states near the Fermi level: hole-like N-*p* states at IFB and IFB-1 (orange) and electron-like Sc-*d* at IFA and IFA-1 (green).

Supporting information

DOI: 10.1002/((please add manuscript number))
Article type: Communication

Oxy-nitride Multilayers as a Platform for Parallel Nanoscale Electron-Hole Conductors: MgO/ScN(111)

*Antia S. Botana, Victor Pardo, and Warren E. Pickett**

Dr. Antia S. Botana and Prof. Warren E. Pickett

Department of Physics, University of California Davis, Davis, California 95616, USA

Email: wepickett@ucdavis.edu

Dr. Victor Pardo

Departamento de Fisica Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

Instituto de Investigacions Tecnoloxicas, Universidade de Santiago de Compostela, E-15782 Campus Sur s/n, Santiago de Compostela, Spain.

Early density functional theory-based calculations employing the LDA[1] or Xα[2] approximations predicted ScN to be a semimetal. In order to overcome the well-known underestimation of the LDA band gap, more advanced exact exchange and screened exchange calculations have been performed and showed that ScN is a semiconductor with an indirect Γ-

X band gap, consistent with experiments. However, the calculated band gap of 1.6 eV is significantly larger than the experimental value of 0.9 eV.[3] LDA/GGA-PBE/GGA-WC+*U* [4] calculations using a *U* value as high as 6 eV are only able to open an indirect gap of 0.40 to 0.55 eV, respectively, far from the one determined experimentally.[5]

LDA calculations complemented with estimated quasiparticle corrections and calculations of the optical response give an indirect band gap of 0.9 eV with a first direct gap at *X* of 2 eV. [6]

G_0W_0 quasiparticle calculations predict ScN to have an indirect band gap between Γ-*X* of 0.99 eV.[7] Also hybrid functionals show the opening of a band gap of 0.9 eV.[8]

Figure S1 shows the band structure with band character plot (N and Sc character highlighted) for ScN obtained within TB-mBJ (see the Methods section in the main text for details). Taking the usual valence for N, the average valence for the Sc cations is +3 (d^0). The band gap is formed between occupied N-*2p* and unoccupied Sc-*3d* states and the experimental value of the gap is reproduced: an indirect band gap of 1.0 eV between Γ-*X* is obtained as well as the direct gap of 2.1 eV at *X*.

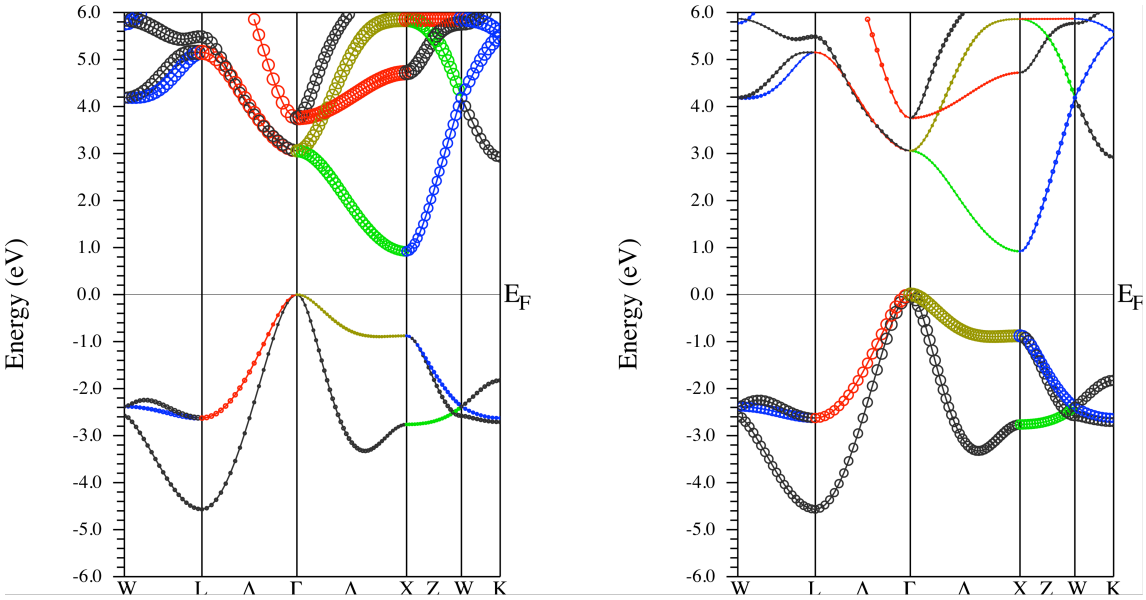

Figure S1. Band structure with orbital character shown by circle size, for ScN using the TB-mBJ potential. Left panel: Sc *3d*; right panel: N *2p*.

Figure S2 shows the band structures with band character plot that complement Fig. 2 in the main text that shows only the DOS. The bands crossing the Fermi level are indeed N-*p* at IFB and Sc-*d* at the IFA.

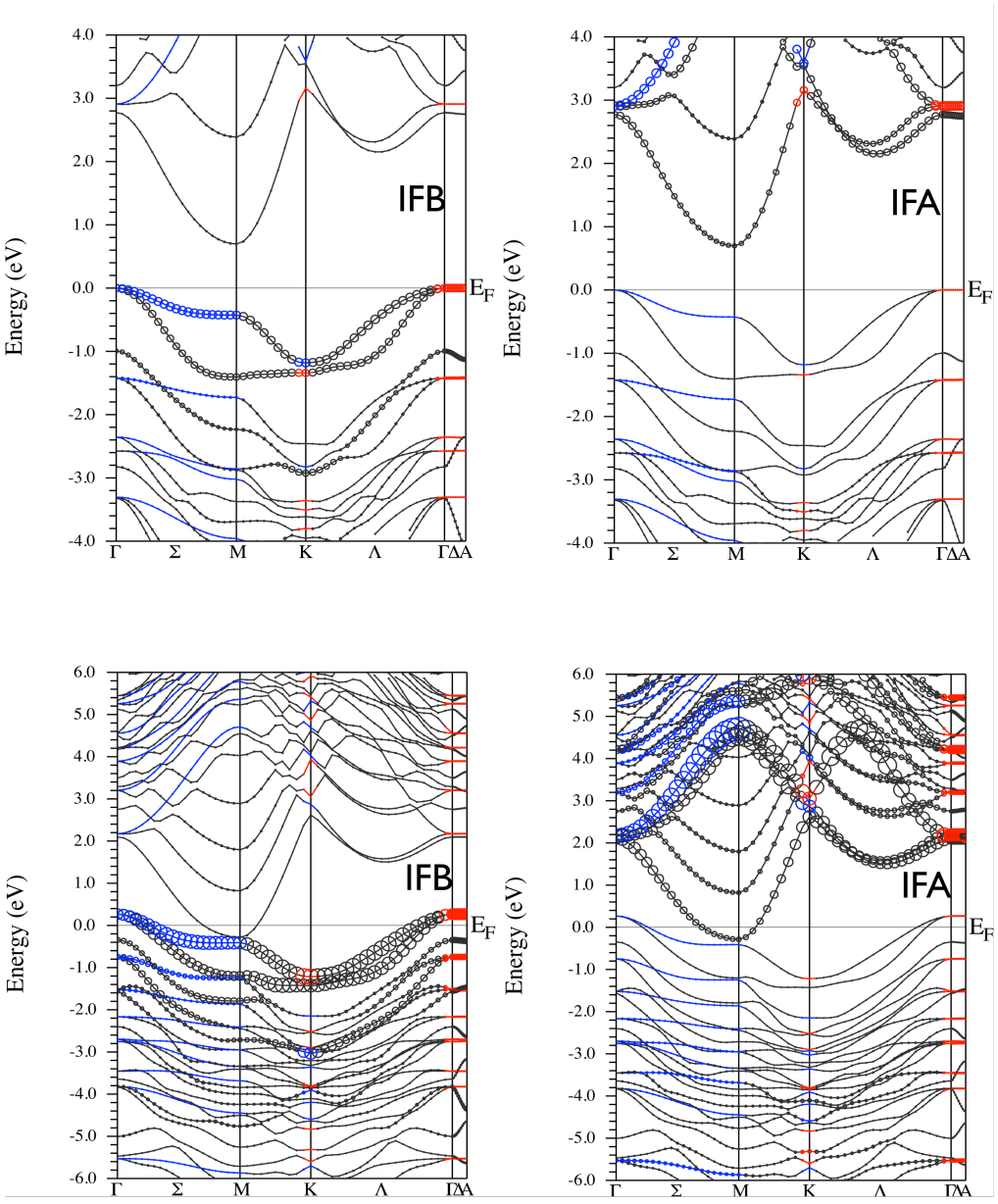

Figure S2. Band structure with band character plot for MgO/ScN (111) multilayers. Sc-*d* atom at IFA(right) and N-*p* levels at IFB (left) for ScN/MgO(111) multilayers three (top panel) and six (bottom panel) ScN-layers-thick.

These bands give rise to the nearly circular Fermi surfaces coming from the electron and hole pockets, as discussed in the main text, as can be seen in **Figure S3.**

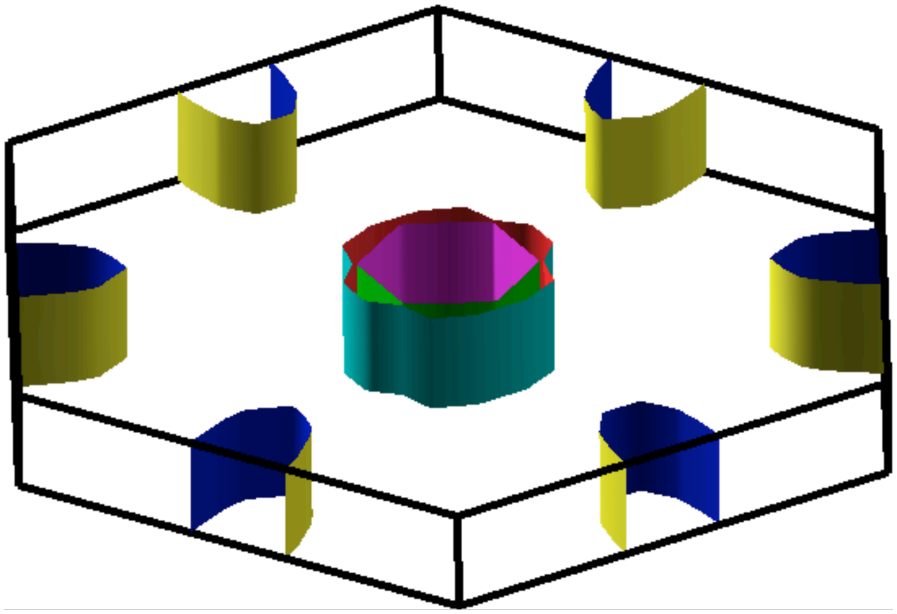

Figure S3. Fermi surface plots for hole and electron pockets obtained for ScN/MgO(111) multilayers 6 ScN layers thick the nearly circular hole pocket is centered at Γ whereas the nearly eliptical Fermi surfaces centered at the hexagonal zone face *M* point correspond to the electron pocket.

References for the Supporting Information.

[1] R. Monnier, J. Rhyner, T. M. Rice, and D. D. Koelling, Phys. Rev. B 31, 5554 (1985).

[2] a) P. Neckel, R. Rastl, P. Eibler, P. Weinberger, and K. Schwarz, J. Phys. C 9, 579 (1976); b) R. Eibler, M. Dorrer, and A. Neckel, Theor. Chim. Acta 63, 133 (1983).

[3] D. Gall, M. Stdele, K. Jrrendahl, I. Petrov, P. Desjardins, R. T. Haasch, T.-Y. Lee, and J. E. Greene, Phys. Rev. B 63, 125119 (2001).

[4] A. Lichtenstein, V. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).

[5] M. Abu-Jafar, A. Abu-Labdeh, and M. El-Hasan, Computational Materials Science 50, 269 (2010).

[6] W. R. L. Lambrecht, Phys. Rev. B 62, 045204 (2000).

[7] A. Qteish, P. Rinke, M. Sche_er, and J. Neugebauer, Phys. Rev. B 74, 245208 (2006).

[8] S. Kerdsongpanya, B. Alling, and P. Eklund, Phys. Rev. B 86, 195140 (2012).