The role of the band gaps in reconstruction of polar surfaces and interfaces

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Density functional theory applied to a simple ionic material, MgO, is used as a model system to clarify several aspects of electronic driven mechanism to compensate for the diverging electrostatic potential in the polar structures. We demonstrate that in the stoichiometric free standing films, the electronic reconstruction is limited by the band gap. This produces a residual electric field in the bulk of the sample which is extremely sensitive to tiny deviations in electron transfer between two surfaces of the slab. In heterostructures, the band gap is replaced by a new effective energy scale set by the band alignment of its component. This changes the reconstruction pathways so that the electronic mechanism can benefit from the smallest energy scale possible.

Beyond a doubt, the electrostatic potential plays a fundamental role in the surface and bulk properties of virtually any ionic material. It has been long recognized as the driving force behind the so-called polar catastrophe that controls the physics and chemistry of polar surfaces and interfaces. A prominent example is a discovery of a 2D electron gas at the interface between LaAlO

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and SrTiO

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. In the bulk, each one of these perovskites is an insulator with large conductivity gap of 5.6 and 3.25eV, respectively. However, when the two are combined in a heterostructure such that the (001) plane becomes an interface, a new metallic state is created. Several proposals have been put forward to explain the effects. It is argued that the large sheet charge density could be a result of Oxygen vacancies formed in SrTiO

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during the growth process followed by the spatial separation between the charge compensating electrons and the vacancies. Yoshimatsu et al. suggested the conventional band bending mechanism based on the observation of the core level shifts seen in photoelectron spectroscopy for LaO-TiO

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interface in a soft x-ray regime. The mechanism of particular interest is that of electronic reconstruction resulting in self doping of the interface layers with carrier density and mobility that are much higher than currently achieved in conventional semiconductors. The feasibility of electronic reconstruction scenario is currently under extensive investigation from experimental as well as theoretical standpoint. Here we have examined the role played by the band structure in electronic reconstruction of polar surfaces and interfaces. To avoid unnecessary complexity, we focus on simple materials keeping all other degrees of freedom frozen. We chose magnesium oxide because of simple crystal structure and high ionicity even though we do not expect MgO to electronically reconstruct because of the large cost in energy due to the large band gap.

According to Tasker’s classification scheme, the (001) surface of LaAlO

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and (111) surface of MgO belong to type 3 polar termination of an ionic crystal and thus should not exist without a major reconstruction. The instability occurs due to accumulation of the electrostatic potential in the direction parallel to the surface normal. Each unit cell contributes the same potential drop resulting in the electrostatic potential diverging with the film thickness. By virtue of its construction, only stoichiometric films with unlike polar terminations (Fig1(a)) exhibit a divergent potential inside the material which drives the surface/interface reconstruction. In the non-stoichiometric structures with both film surfaces alike, the surface electronic structure is governed by the requirement of overall charge neutrality. For example, a defect-free (111) MgO film terminated on both sides with Mg is expected to be metallic in band theory because there is not enough Oxygen in the system to fully oxidize the Magnesium. Given the geometry of the structure and the Coulomb repulsion between alike charges, it is clear that the Mg on this surface should be 1+ just like the Mg on the surface of a stoichiometric (111) MgO slab in the case of electronic reconstruction. This approach kind of bypasses rather than treats the polar catastrophe.

FIG. 1: An artist’s concept of charge neutral stoichiometric (a) and non-stoichiometric (b) slabs. Σ is a planar charge density (Q/A). The arrows depict electron transfer due to electronic reconstruction (σ) and charge density redistribution at the interface (δ) due to the band structure effects.
issue but is a convenient approximation to get insight into the properties of excess charge density at each interface separately that might not be feasible otherwise\cite{9,18}. Note that the term non-stoichiometric is used by us in a rather specific sense and refers to the systems in which the number of positive and negative charged atomic layers differs by one. It does not include formation of point defects such as vacancies nor adsorption of the foreign species on the surface.

Unlike type 3, the non-polar crystal truncations are a single boundary problem. Here, the properties are determined by the discontinuity in the crystal potential at a single interface with another material or vacuum. For example, the Shockley surface state on (111) surfaces of simple metals such as Cu, Ag or Au is a result of such discontinuity\cite{19}. In a case of charge neutral (type 1) surfaces of the ionic materials, it is the disruption of the Madelung potential and the change in the local symmetry and coordination numbers that governs a change in the electronic structure of a material at the surface. Some layered structures such as realized in TiS$_2$ where Ti$^{4+}$ layer is sandwiched between two S$^{2-}$ layers do exhibit a charged surface (e.g. (001) surface) but just like type 1 surfaces bear no dipole moment in the unit cell in a direction perpendicular to the surface. Hence, the surface energy is always finite.

What are the solutions to the polar catastrophe generated by a polar crystal truncation? As suggested by recent density functional calculations, a simple solution might prevail when the films are stoichiometric and only a few layers thick\cite{20,21}. The prescription is to reduce the dipole moment in each unit volume by essentially converting the two adjacent planes (e.g. Mg (2+) and O (2-) (111) planes in MgO) into one almost charge neutral plane with vanishingly small dipole. Similar behavior was found in the calculations of thin LaAlO$_3$ overlayers on a SrTiO$_3$ substrate\cite{17}. These findings are consistent with the observation of a critical thickness in LaAlO$_3$/SrTiO$_3$ heterostructures for metallic behaviour of the interface\cite{22}. There are, however, other plausible pathways whose contributions to the total energy of the system are independent of the film thickness.

Basic electrostatic arguments suggest that the divergence of the electrostatic potential can be cured if the charge on the top and bottom surfaces is reduced to half of that of the corresponding layers in the bulk\cite{23}. Adsorption of a monolayer of foreign ions is, perhaps, the easiest way to achieve this without destroying the charge neutrality or introducing a significant structural modification on the surface. A notable example is a growth of $\alpha$-MnS single crystals using iodine as a transport agent in chemical transport method\cite{24}. The crystals are found to exhibit Mn terminated (111) faces with a monolayer of I$^-$ on top. Note, the crystal structure of $\alpha$-MnS is rock salt and hence this termination should be otherwise-unstable. As another example, the hydroxyl groups have been observed on the polar surfaces of divalent oxide films\cite{25,29}.

The surface charge can also be altered by vacancies. For example, the recently discovered high temperature superconductor BaFe$_2$As$_2$ has a nominal layered structure stabilized by the extremely large electronic polarizability of pnictogens\cite{30,32}. It consists of negatively charged (001) FeAs sandwiches alternated with the Ba 1+ layers that generates a polar surface when the material is cleaved parallel to the layers. Scanning tunnelling microscopy studies suggest that the surface generated by cleaving is the Ba-terminated surface with every other Ba missing\cite{33,34}. A more involved defect structure is often discussed in relation to (111) surfaces of the ionic materials with a rock salt crystal structure. For example, the so-call octopolar reconstruction is one in which 3/4 of the layers of octopolar reconstruction on (111) surfaces of MgO are exactly balanced with respect to charges of layers underneath. Scanning tunnelling microscopy studies suggest that the surface generated by cleaving is the Ba-terminated surface with every other Ba missing\cite{33,34}. A more involved defect structure is often discussed in relation to (111) surfaces of the ionic materials with a rock salt crystal structure. For example, the so-call octopolar reconstruction is one in which 3/4 of the layers of octopolar reconstruction on (111) surfaces of MgO are exactly balanced with respect to charges of layers underneath. Scanning tunnelling microscopy studies suggest that the surface generated by cleaving is the Ba-terminated surface with every other Ba missing\cite{33,34}. A more involved defect structure is often discussed in relation to (111) surfaces of the ionic materials with a rock salt crystal structure. For example, the so-call octopolar reconstruction is one in which 3/4 of the layers of octopolar reconstruction on (111) surfaces of MgO are exactly balanced with respect to charges of layers underneath. Scanning tunnelling microscopy studies suggest that the surface generated by cleaving is the Ba-terminated surface with every other Ba missing\cite{33,34}. A more involved defect structure is often discussed in relation to (111) surfaces of the ionic materials with a rock salt crystal structure. For example, the so-call octopolar reconstruction is one in which 3/4 of the layers of octopolar reconstruction on (111) surfaces of MgO are exactly balanced with respect to charges of layers underneath. Scanning tunnelling microscopy studies suggest that the surface generated by cleaving is the Ba-terminated surface with every other Ba missing\cite{33,34}.

Electronic reconstruction is yet another compensation mechanism. This mechanism reminds us of the Zener breakdown in which electronic tunnelling between two interfaces occurs when the external electric field exceeds the critical value imposed by the band gap of the dielectric\cite{36}. There is, however, an important difference between Zener theory and polar catastrophe. In the latter case, the electric field is an intrinsic feature of an uncompensated film and should vanish if surface charges are exactly balanced with respect to charges of layers underneath.

Let us consider a simple capacitor like model of a stack of N alternating charged planes with the charge density $\Sigma$ and separation $d$ as shown in Fig.1(a). The potential difference between two interfaces is given by

$$V_{\text{slab}} = \frac{\sigma}{2\epsilon_0} (2N - 1)d + \frac{\Sigma}{2\epsilon_0}d$$

(1)

where $\sigma$ is the electron transfer between two interfaces (0 $\leq$ $\sigma$ $\leq$ $\Sigma$). Here, we refer to the surface as the interface. The second term is the bulk electrostatic potential, $V_{\text{bulk}}$. When $\sigma = 0$, $V_{\text{slab}}$ is simply equal to

\textbf{FIG. 2:} Schematic representation of the octopolar reconstruction of polar (111) surface of an ionic material with rock-salt structure.
FIG. 3: GGA layer projected Mg (a) and O (b) density of states for 18 bilayer thick MgO (111) slab. The zero of energy is at the Fermi energy, $E_F$. The arrows depict the lower (electrons) and upper (holes) limits in the integration about $E_F$ used to calculate charge densities. Reconstructed charge distribution (c) and planar averaged total potential (d) in the slab as a function of distance $z$ in direction parallel to surface normal. The residual electric field as a function of slab thickness (insert in (d)). A comparison between bulk and slab total density of states (e).

twice the number of bilayers times the potential drop in the bulk material (e.g., potential drop between adjacent Mg and O (111) planes in the unit cell of MgO). To put it in perspective, the 4.3 nm thick (111) film of MgO (18 bilayers) would experience an unsustainable 1030.7 V potential across it. It is only about a factor of 2.4 smaller in LaAlO$_3$ (001) slab consisting of the same number of atomic layers (429.5 V). Nevertheless, when the charge density on the both interfaces is reduced to a half ($\sigma = \frac{1}{2} \Sigma$), the potential inside the slab equals the bulk potential and the electric field averages out to zero suggesting that the properties of fully charge compensated film are, interface layers aside, representative of that in the bulk. While capturing the basic electrostatics, such a simple model is lacking some key ingredients. Neglecting the polarizability effects, it is clear that redistribution of the electronic charge between two unlike interfaces requires an excitation across the band gap.

This brings us to the main subject of the paper: the role played by the band gap in electronic reconstruction of polar surfaces and interfaces. Let us define a quantity $\delta V = V_{\text{slab}} - V_{\text{bulk}}$ as a measure of the divergence in the electrostatic potential of the polar slab. As long as $\delta V$ is larger than the band gap, the electrons would have to carry the compensating charge from one interface to another until $\delta V = \Delta$ condition is fulfilled. Neglecting the band structure effects, the electron transfer is given by $q = \frac{1}{2} Q - \frac{\Delta}{2N-1} d$, where $Q$ is a charge per unit area $A$ of the atomic plane in the bulk. Note that $\Delta$ decreases the amount of charge transfer and only in the limit of very thick films ($N \rightarrow \infty$) the films are fully electronically reconstructed ($q = \frac{1}{2} Q$). Using 7.8 eV band gap and assuming fully ionic charges, we estimate the amount of charge left on the reconstructed surface of 18 bilayers thick MgO (111) slab to be ±1.008e. This corresponds to a transfer of 0.992 electron between two surfaces of the slab. We get ±1.004e surface charge when the gap is reduced to DFT value of 4.5 eV. The incomplete reconstruction leaves behind the residual electric field of $\Delta/(2N-1)d$. 

The field is greater for the larger band-gap materials and can alter the crystal structure of very thin films as was demonstrated recently by the DFT calculations of lattice relaxation in various polar films\(^{17,20,21,35}\). Note that there is no internal field in the non-stoichiometric case.

Turning the discussion to the results of our DFT studies, we note that MgO has the rock salt crystal structure with a lattice constant of 4.213Å. It is a perfect dielectric with the band gap of 7.8eV\(^{37,38}\). Using experimental lattice constant, we get the band gap of 4.5 eV in agreement with previous density functional calculations\(^{39}\). The MgO electronic structure is calculated using the pseudopotential DFT code SIESTA\(^{40}\) with the norm-conserving Troullier-Martins pseudopotentials\(^{41}\) and the non-polar term set of double-\(\zeta\) quality for \(s-p\) and single-\(\zeta\) for \(d\)-orbitals. The exchange and correlation effects are treated within the generalized gradient approximation (GGA), after Perdew et al\(^{42}\). In the slab calculations, we adopt an ideal bulk crystal structure and periodic slab geometry with 100Å separation between the slabs. The effects of periodic boundary conditions will be discussed latter. The stoichiometric slabs consisting of 6-18 MgO bilayers are used throughout this study to address the polar catastrophe. No lattice relaxation has been performed in order to isolate the effect due to electronic reconstruction.

Figures 3 (a) and (b) show the layer projected density of states for 18 bilayers thick MgO film terminated with Mg layer on one side and Oxygen on the other. The presence of the electric field is clearly evident from the shifts in the layer projected density of states and the slope of planar averaged total potential shown in Fig. 3(d). To find the exact amount of charge transferred between two surfaces, we calculate the two dimensional electron density of the slab as a function of the distance in a direction perpendicular to the slab. The electron and hole densities are calculated separately as the integrals over the ab-plane and over the energy from -3eV to \(E_F\) (electron) and from \(E_F\) to +2eV (hole) as depicted by the arrows in Fig. 3 (a) and (b), respectively. To select the surface related contributions, the densities are truncated with a cutoff value of \(10^{-4}\)\,e/Å\(^2\). The apparent difference in spatial distribution of hole and electron densities as seen in Fig. 3(c) is due to the spatial extend and orientation of the atomic orbitals these particles are in. The electrons occupy rather extended and isotropic Mg 3s orbitals whereas the holes are in in-plane O 2p states. This is a result of the Hartree density-density repulsion between the O 2p electrons which is at its minimum when the holes are confined to the surface. Further integration over \(z\) reveals 0.9860±2×10\(^{-4}\) electron transfer (\(q\)). It is remarkable how close it is to ±1 reconstruction expected for an ideal slab in which Mg and O are fully ionic with charges ±2. Reduction in slab thickness results in a persistent decrease in \(q\) as shown in fig.4. A deviation from the estimates given above can be attributed to actual electron density distribution and the band structure effects being not accounted for in the ionic model.

As one can see in Fig. 3(c), the electron density on the Mg surface is rather extended in a direction away from the slab changing the electrostatic potential in the slab. Therefore, the expression for electron transfer needs to be modified. It is easy to show that, for this particular case, \(q\) is given by

\[
q = \frac{Q/2 - \Delta \epsilon_0 A/D}{1 + d_0/D} \quad (2)
\]

where \(D = (2N - 1)d\) and \(d_0\) is the distance from Mg surface to the mean of the electron density in vacuum. Note that the equation reduces to that given above in a limit of \(d_0 = 0\). Using the 3.6V residual potential found in DFT calculation of 18 bilayer thick slab, we get \(Q = 1.997 \pm 0.003\,e\) and \(d_0 = 0.39 \pm 0.03\,Å\) by fitting eq.2 to the DFT data for electron transfer obtained for various slab thicknesses.

Due to the residual electrostatic potential, the total density of states is broadened to, approximately, the total width of that in the bulk plus the gap energy. The effect is most evident in a case of O 2s states whose bandwidths are increased from 2eV in the bulk to about 5eV as shown in Fig. 3(e) suggesting that the spectroscopy of polar films could be very different from the bulk or films with non-polar terminations.

What about the periodic boundary condition? Since the slab is charge neutral there should be no electric field outside of the slab. The periodic boundary condition creates an artificial potential drop with the slope proportional to 1/\(D_V\) where \(D_V\) is the distance between the slabs. This is analogous to non polar slabs with unlike terminations such as SrO and TiO\(_2\) surfaces in SrTiO\(_3\) (001) slab. This is often avoided by treating the surfaces separately e.g. SrTiO\(_3\) (001) slab terminated with SrO layer on both sides. It is not an option in a case of polar slabs. One can wonder if an artifact due to PBC has any influence on the electronic structure of polar films. A simple way to resolve PBC problem is to create a double
LaAlO$_3$ faces are essential part of any heterostructure such as grown without the substrate. Furthermore, the inter-electronic reconstruction is the films band gap. It condition.

The residual potential inside the slab is about 3.6V. We conclude that for sufficiently large $D_V$ the electronic structure of the film calculated in a single slab geometry is not affected significantly by the periodic boundary condition.

In free-standing films, the main cause for incomplete electronic reconstruction is the films band gap. It is, however, a conceptual system since films are never grown without the substrate. Furthermore, the interfaces are essential part of any heterostructure such as LaAlO$_3$/SrTiO$_3$. One can wonder if an interface with non-polar material can alter the electronic reconstruction of the polar films. Neglecting the band structure effects, this question leads to reexamination of the energy scales involved in the process. It is clear that, as long as the electronic structure on the non-polar side of the interface is such that it can provide states in the band gap of the polar one, it would have to be a part of the electronic reconstruction. Nevertheless, the charge redistribution within a single interface can not cure the polar catastrophe. Electrostatics requires that both interfaces participate in the same manner as in a free standing film.

Let us now examine the electronic structure of a stoichiometric MgO (111) film on the surface of a metal, namely, aluminum. To keep the discussion coherent, we assume an ideal crystal structure and the lattice constant of MgO (Al is isotropically expanded). The lattice mismatch between Al and MgO is 3.9 percent. The structure is modelled by 18 bilayers of MgO and the same number of monolayers of Al in a single slab geometry with 100Å of vacuum. The interface distances are chosen according to the minimum in the total energy as a function of MgO-Al distance. For the O-Al interface, we find that the separation is 1.44Å whereas it is substantially larger in a case of Mg-Al contact, 2.4Å. Quick inspection of layer projected DOS shown in Fig. 6 reveals that (i) the MgO surface projected DOS is very close to that in a free standing film (fig.3); (ii) the residual potential is 4.0V in MgO/Al slab containing Mg-Al interface and it is reduced to zero in the case of an O-Al contact layer; (iii) Al surface projected density of states is not affected by the interface with MgO.

It is impossible to accurately predict the band alignment in the case of polar interface because the films are always reconstructed electronically in the calculations. However, the difference in $\delta V$ can be understood if the Fermi energy of Al was closer to the conduction band rather than the top of valence band of MgO. If that is the case, the redistribution of the charge between Mg surface and O-Al interface would necessitate the energy scale that is less than a half of the band gap which translates into smaller $\delta V$ and increases the electron transfer. This is exactly what we find. It is clear that having Al electronic states in the band gap of MgO helps to reduce the energy needed to reconstruct electronically because they provide the reservoir of the compensating charge at a fraction of the cost. The end result depends, however, on the film orientation (O vs Mg contact) and layer spacing at the interface. For example, we find that the total
energy of the film with Mg-Al contact is about 3.1eV higher as compared to O-Al contact which is simply another evidence of much larger energy scale involved in the electronic reconstruction of the film. Again, we stress that due to electrostatic nature of the problem both surface and interface are strongly coupled via the electrostatic potential. This drives the electron transfer from Oxygen surface into Mg-Al interface that, in this particular configuration, costs almost as much as the band gap energy and leads to the residual potential which is nearly independent on the interface spacing, Fig. 7. The switch to another geometry allows to utilize much smaller energy scale and reduce the residual potential to zero at optimal O-Al distance. Of course, when this distance is large, the system is no longer coupled and the electronic reconstruction pathway is independent on the Al substrate. So, the reconstruction energy scale is, again, the band gap of MgO.

To further demonstrate the interplay between the structure and the energy in electronic reconstruction pathways, we calculate the electronic structure of MgO (111) film sandwiched between two Al slabs (Al$_{12}$/MgO)$_{12}$/Al$_{12}$). The interface distances are chosen to be equal to that found in MgO/Al slab calculations. Figure 8 shows the layer projected density of states and the planar integrated valence electron density difference defined as \( \Delta \rho(z) = \rho_{\text{Al}/\text{MgO}/\text{Al}}(z) - \rho_{\text{Al}}(z) - \rho_{\text{MgO}}(z) \). Comparing to Fig. 6, it is clear that the MgO projected DOS is very similar to that in MgO/O-Al/Al slab with the exception of the Mg surface projected DOS. In particular, there is no shift in MgO DOS that suggests that the structure is fully compensated electronically. The electron density difference plotted in Fig.8(b) as a function of distance \( z \) in a direction parallel to interface normal illustrates the role of Al band structure in the reconstruction pathway. As in other structures considered, the electron transfer is across the MgO slab but it is, to a large extent, Al density that participate in the process. This reduces the double interface energy \( E_{\text{dint}} \) to 1.92eV as compared to the slab surface energy \( E_{\text{SSSE}} \) of 6.02eV in a free standing MgO. The \( E_{\text{dint}} \) is given by

\[
E_{\text{dint}} = E_{\text{tot}}(\text{Al/MgO/Al}) - N E_{\text{tot}}(\text{MgO bulk}) - M E_{\text{tot}}(\text{Al bulk}) - 2 E_{\text{surf}}(\text{Al})
\]

where \( N \) (resp. \( M \)) is the number of formula units in Al (MgO) slab; \( E_{\text{tot}} \) is the respective total energy; \( E_{\text{surf}}(\text{Al}) \) is surface energy calculated for 12 monolayer thick Al (111) slab using MgO lattice constant (0.42eV). Correspondingly, the slab surface energy is \( E_{\text{SSSE}} = E_{\text{tot}}(\text{MgO slab}) - M E_{\text{tot}}(\text{MgO bulk}) \).

In conclusion, we demonstrate that the shifts in the DOS of polar systems are extremely sensitive to tiny deviations in electron transfer involved in the electronic reconstruction mechanism. They are not the signatures of electronic reconstruction and only tell us about its incompleteness. It is a result of an effective energy scale which is required in order for charge to be transferred between the oppositely charged interfaces. In a free standing film, this energy scale is set by the band gap modified to some degree to incorporate the band structure effects. At interfaces, it is determined by the band alignment and it is always the smallest energy possible helping the electronic reconstruction mechanism to be realized more readily in heterostructures as compared to free standing films. Due to high sensitivity of the inner potential variation to the interface charges, one can expect that the interface imperfections such as vacancies or adsorption

- **FIG. 7:** The residual potential in MgO (111) film on the Al substrate as a function of interface spacing \( d_{\text{tot}} \). The solid symbols depict \( d_{\text{tot}} \) corresponding to a minimum in the total energy as a function of \( d_{\text{tot}} \).  

- **FIG. 8:** Left panel - GGA layer projected DOS for Al$_{12}$/MgO$_{12}$/Al$_{12}$ slab. The zero of energy is at the Fermi energy. Middle panel - valence electron difference \( \Delta \rho \) as a function of distance \( z \) in direction parallel to interface normal \( \Delta \rho(z) = \rho_{\text{Al}/\text{MgO}/\text{Al}}(z) - \rho_{\text{Al}}(z) - \rho_{\text{MgO}}(z) \). The oscillations inside MgO fragment of the structure are due to incomplete electronic reconstruction in free standing MgO (111) film. The oscillations at the interfaces are due to the change in reconstructed electron (hole) density distribution as compared to single MgO slab. Right panel - an illustration of the change in spatial distribution of compensating electron and hole densities due to interface with Al. The large oscillations at the interfaces in (b) are primarily due to readjustment of the compensating densities as compared free standing film.
of foreign species can reduce significantly the residual electrostatic potential even though the electron transfer energy scale of pure material is still rather large43. This can, in principle, reconcile theory and the results of x-ray photoelectron spectroscopy measurements in which no inner potential variation was found13,16,24,44–46. Furthermore, bulk impurity states energetically distributed across the band gap can somewhat modify the charge distribution at the interface in a fashion similar to conventional semiconductor P-N junctions.

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