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Theory of Ferroelectricity Incorporating a Finite Bandgap : Surface Phase, Ferroelectric Metal, Size Effect

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Reexamining the concepts of the semiconductor and the size effect, we aim to construct a new understanding of ferroelectric perovskites, with stress on the field effect. Most ferroelectric perovskites have a finite band gaps of 3 to 4 eV. If this fact is incorporated in a conventional theoretical framework, various experimental results can be explained. Instead of estimating the smallest limit of size for a stable ferroelectric phase as conventionally pursued, we propose to investigate the ferroelectric surface and the miniature ferroelectric as a new phase possessing potentially beneficial properties.

Keywords : ferroelectric, surface, size effect, field effect, electron gas

1. INTORODUCTION

Ideal ferroelectrics have been modeled as insulators, i.e., infinite band gap materials, having a spontaneous polarization (*Ps*). Based on this assumption, theories for the finite size effect (FSE), the domain configuration, and the depolarization field instability have been proposed. However, most ferroelectric perovskites have a finite band gaps of 3 to 4 eV. An exact inclusion of the finite band gap effect changes drastically conventional understanding of FSE and others. The conclusions extracted from the present approach are consistent with recent experimental results.

Additionally, the miniature ferroelectric like nm-scale particulate or ultrathin film is shown to be too boundary-sensitive to treat as a simple material of a small limit as done in a conventional condensed matter physics. Instead, we propose that the properties of such a small ferroelectric should be defined in an appropriate heterostructure containing it or in an inhomogeneous structured material.

Starting from the examination of the concept of the semiconductor, we redefine FSE in ferroelectric, and suggest a new phenomena at ferroelectric surface. The theory suggest an existence of two-dimensional electron gas at a clean free surface of ferroelectric and its strong coupling to the lattice and, especially, *Ps*. Such a layer should be regarded as a new phase.

2. SEMICONDUCTOR VS. INSULATOR

Si and GaAs have energy bandgaps (*Eg*) of 1-2 eV and are regarded as semiconductors. If the electron correlation and a weak localization are disregarded, all the semiconductors are insulators, i.e., band insulators at low-temperature (*T*). Therefore, it may be artificial to distinguish the semiconductor from the insulator.

$BaTiO_3$ and other oxides are often said to become semiconductors, when they are doped. This is an illogical expression. If $BaTiO_3$ is a band insulator and conducts current reasonably well by doping, an undoped $BaTiO_3$ should also be regarded as a semiconductor.

Where comes this misunderstanding ? It

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originates from a huge difference between Si and $BaTiO_3$ in doping dependence of the resistivity and the mobility. The low mobility in $BaTiO_3$ is likely due to the strong interaction of electron with lattice, i.e., polaron. Furthermore, Si can have shallow donor and acceptor level, while $BaTiO_3$ does not.

However, all these differences seem inessential, and the distinction between the semiconductor and the insulator seem to be judged based on the magnitude of *Eg*.

3. EFFECT OF BANDGAP ON FIELD EFFECT

When a static electric field *E* is applied to a material, it is screened by the deformation of the lattice and the change of atomic positions (dielectric response of ion), the accumulation of ion (ion segregation), the deformation of electrons bound to ions (dielectric response of electron), and the accumulation of electron.

The mode of screening depends on the kind of materials, *T*, and time scale τ. We concentrate on *T* and the time scale τ_i for which we can neglect the ion segregation. In a metal with *Eg* = 0, *E* is perfectly screened by electrons for the length longer than the Thomas-Fermi screening length. In an ordinary semiconductor with a modest *Eg*, *E* is partially screened mostly by electrons and partly by a dielectric response. In a typical insulator with a large *Eg*, only a small fraction of *E* is screened, which is accomplished by a dielectric response.

E can generate carriers in insulators, if the time scale τ_e for the carrier generation is sufficiently shorter than τ_i and *E* is not small in comparison with *Eg* divided by a typical length scale. For the carrier generation, *E* is also required not too large, because too a large *E* should shorten τ_i or promote the ionic segregation. Namely, the carrier generation requires $\tau_e < \tau < \tau_i$ or that *E* bends the band in a magnitude similar to *Eg* and does not still change much the lattice and the ionic motion.

4. FIELD EFFECT IN FERROELECTRIC

The field effect transistor (FET) uses a metal/ SiO_2/Si structure (M/I/S, M: metal, I : insulator, S: semiconductor). This structure satisfies the requirement in Sec.3. The M/I/S-FET utilizes the fact that *E* acting on SiO_2 and Si bends the band of Si and accumulates carriers in Si.

The reason that only in Si, the band bends and carriers accumulate is *Eg* of SiO_2 larger than *Eg* of Si. We may generalize the result of MIS: If we disregard the discussions in Sec.3, we conclude that in M/S'/S, *E* applied across S'/S bends the band of S and generates carriers almost solely in S for *Eg* of S' > *Eg* of S.

Bound charges at the S'/S interface yields the same effect for *Eg* of S' > *Eg* of S. They bend the band of S and accumulate carriers almost solely in S as concluded by Vul et al.[1] The extension of the conclusion is that bound charges at the I'/I S interface yields the same effect for *Eg* of I' > *Eg* of I. Carrier generation by *E* is an essence of the semiconductor. Therefore, this implies that the semiconductivity is not determined by the absolute value of *Eg* but the relative value of *Eg* compared with *Eg* of contacting material.

In view of the discussion in Sec.3, this conclusion holds only partially. The effects of the lattice deformation, and the dielectric response, and the ionic motion should be consistently treated along with the effect of carriers.

Perovskite oxides with *Eg* = 2eV, e.g., a parent phase of a high temperature superconductor showed carrier accumulation by the field that was retained for a long time.[2] Additionally, experimental results supporting the band bending and its interaction with *P*s are increasing.[3]

Therefore, we assume that in ferroelectric oxides like $BaTiO_3$ and $PbTiO_3$, the condition $\tau_e < \tau < \tau_i$ is satisfied.

Namely, we treat the field effect in the ferroelectric oxides by balancing the screening by the carrier generation and the dielectric response by the lattice deformation. They are regarded as semiconductors having a special lattice deformation. Here, we neglected the effect of the electron orbital deformation, because it corresponds to the optical dielectric constant that is of order 5.

5. FINITE SIZE EFFECT (FSE)

The crystallographic properties and the electronic state at the surface are different from the bulk in all the materials. With decreasing dimension, the effect of the surface governs gradually the property of the materials. This is one of the causes of FSE. Secondly, the crystallographic properties are determined both by local atomic properties and by long range forces. Therefore, the crystallographic properties of a small dimension can be different from those of the large dimension, even if the effect of the surface is absent.

Many works on FSE of various materials are already done. Among them, the FSE of the superconductivity and the magnetism is of a fundamental interest, because they originate from the electric correlation. The changes of crystallographic properties alter everything including the electronic state. Therefore, enormous efforts are done to keep the crystallographic parameters unchanged. For this purpose, epitaxial structures are extensively used. As a result of such efforts, the reduction of the Curie T (Tc) and the susceptibility with thickness is negligible down to a few monolayer thickness, e.g., in Gd/W system.

6. SIZE EFFECT IN FERROELECTRIC

Numerous works on the ferroelectric FSE are done. Because the change of crystallographic properties itself is one of the essences of its phase transition, the effort to suppress this change has been scarcely performed in contrast with the studies of other systems. This means that the studies of FSE in ferroelectric loses a standard for judging whether samples are correctly prepared. Indeed, the minimum size l_c for the existence of stable phase is far larger than those of other systems and has been constantly decreasing until now. Theories tried to explain the origin of the large l_c, usually based on an unscreened E.

For example, nm-sized powders for the ferroelectric FSE study have usually many defects, especially, at the surface. These defects change also the crystallographic properties. Many researchers discuss the FSE based on the crystallographic parameters of such powders. However, it seems impossible to judge whether such defects and the change crystallographic parameters are limited by the sample preparation or by a long-range interaction inducing the ferroelectricity.

Use of single-crystal epitaxial structures can remove this ambiguity, although it restricts the spontaneous change of crystallographic properties. Nonetheless, this approach is consistent with the studies of FSE of other systems and can elucidate the effect of the long-range electric interaction. Furthermore, the magnitude of Ps and its switching can be detected, when the ferroelectric is formed on a semiconducting material.

Ferroelectric FSE is sensitive to the boundary condition, i.e., the material contacting with the surface. The conventional theories assume the ferroelectric as a simple insulator. Therefore, E (depolarization field) is reduced only by the domain configuration and the lattice deformation (relaxation). The latter is not much effective for a global stabilization, because dielectric response does not contain a net charge. Therefore, it is expected that the stability of the thin ferroelectric is drastically reduced and the allowable domain configurations are restricted, when a miniature ferroelectric is surrounded by a material having Eg larger than its Eg. The recent experimental results are against this expectation.

As discussed in Sec.4. E can generate electrons in the ferroelectric oxide. The energy for carrier generation is calculated to be relatively small. Therefore, it would be obvious that the effect stabilizes the ferroelectric phase and resolves the restriction of domain configuration as observed experimentally. Details of the first stage theoretical setup, formulation, and the comparisons with experimental data are reported elsewhere.[4]

In our view, lc should be defined using samples free of defects and crystallographic disorders and, therefore, having clean surfaces. For such a freestanding thin platelet in an ultrahigh vacuum, lc is estimated to be below 10nm. The free energy F is only very weakly dependent on the domain width of the stripe domain, meaning the freedom of domain configuration.

In this case, the ferroelectric surface should be regarded as a new phase. The carriers are tightly coupled with Ps and the lattice deformation, as expected from the origin of the carriers,. For example, the change of the domain configuration and Ps accompanies a redistribution of carriers on the ferroelectric surface.

The properties of ferroelectric in a heterostructure seem to be primarily governed by an inhomogeneous and huge stress from the boundaries. Even without stress and the defects at surface, the ultrathin ferroelectric in a heterostructure is under a uniaxial E resulting from the work function difference. Therefore, it tends to be frozen, i.e., polarized in one direction. We may regard it as a size-induced ferroelectric-pyroelectric transition.

7. 2D-GAS AND FERROELECTRIC METAL

The carriers at the ferroelectric surface are estimated to be of order 10 nm and be degenerate for a certain range of parameters (Fig.1). A very rough estimation suggests that a fraction of electrons is quantized. A new kind of 2-dimensional (2-D) electron gas strongly coupled with phonon can possibly appear on the ferroelectric surface.

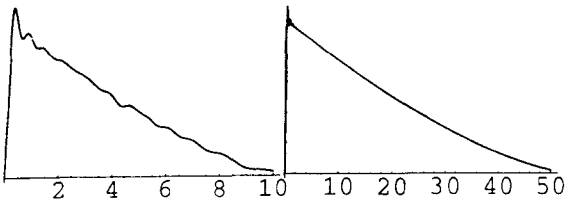

Fig.1 Calculated electron density in 10 nm and 50 nm thick pure $BaTiO_3$. Ordinate is in arbitrary unit. The undulation is due to the quantization of electron waves.

Electrons screen E and stabilize the miniature ferroelectric and the ferroelectric surface. However, they may also screen the electric interaction inducing the ferroelectricity. If this effect does not kill the ferroelectricity, we have an ultrathin metal layer that has an ionic configuration, crystallographic properties, and the ionic interaction of ferroelectric, a ferroelectric metal.

8. CONCLUSION

The surface and the size effect (FSE) of ferroelectric is discussed treating it as electron-lattice charge system. To define the FSE and the ferroelectricity in a heterostructure is not only important for the recent enormous interest for application but also for the fundamental study.

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