

강유전 산화물 계면의 전기화학적 현상 세계 최초 규명

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연구내용

차세대 메모리 및 정보 저장 소자로 주목 받고있는 강유전체 산화물의 자발적 분극(分極)이 계면에서 전기화학적으로 조절되는 현상을 '수차보정 전자 현미경'을 활용하여 원자단위에서 직접 관찰하는데 세계 최초로 성공함.

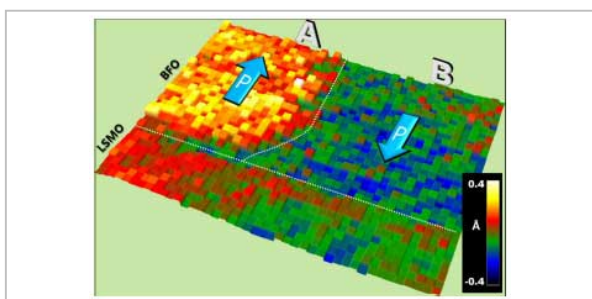
본 연구는 대표적인 다중강성체(多重強性體)인 비스무스페라이트(BiFeO₃) 박막의 계면에서 분극의 방향에 따라 감극 현상이 일어나는 이유가 다름을 원자단위에서 처음으로 규명하였으며, 이를 위해 '수차보정 투과전자현미경'을 활용하여 원자의 위치 변화를 피코미터(pm; 1조분의 1미터=10⁻¹²m)단위로 추적하였고, 계면에서 일어나는 화학적 변화를 직접 관찰하기 위해 '전자에너지손실분광기'를 활용하여 계면에서 바뀌는 금속원소의 산화상태를 직접 이미징 하는데 성공함.

이를 통해 양전하가 모인 계면에선 산소 공공이 재배열함으로써 감극이 이뤄지는 반면 음전하가 모인계면에선 전자-정공의 재배열에 의해 감극이 제어된다는 사실을 발견함.

기대효과

지금까지 '수차보정 전자현미경'을 활용한 연구는 물질의 원자 구조와 구성 성분만 관찰하는데 주로 그쳤는데 이번에 개발된 분석법을 통해 산화물 계 면에서 발생하는 전기화학적 현상을 동시에 관찰 할 수 있게 됨에 따라 그동안 베일에 가려졌던 물 리 현상을 직접 보면서 이해할 수 있게 되어 기초 과학 뿐만 아니라 관련 신소재 개발 연구도 강력한 추진력을 얻게 될 전망이다.

특히 산소 공공은 전자보다 이동속도가 낮기 때문에 외부 전기장을 가해 분극 방향을 바꾸어 주는 분극 스위칭을 할 때 산소 공공의 전기화학적 요소가 스위칭 속도에 더 큰 영향을 미치게 되므로 산 화물 유전체(誘電體)를 메모리 및 기억 소자로 응용할 때 소자의 성능을 예측하는데 중요한 정보를 줄 것으로 기대됨.



[그림 1] 수차보정 전자현미경으로 분석한 비스무스산화철 (BFO 혹은 BiFeO₃)의 유전 분극 맵으로 두 개의 서로 다른 전기 분극 방향을 가진 영역 A와 B가 서로 만나고 있는 모습을 보여준다. 이러한 도메인 배열과 분극의 방향은 전극으로 쓰이는 란타늄스트론튬망간산화물(LSMO 혹은 La_{0.3}Sr_{0.7}MnO₃) 과 비스무스산화철이 붙어있는 계면에서 산소 원자가 빠진 빈 자리가 존재하느냐에 따라 달라진다는 사실을 실험적으로 처음 증명함.

* 그림에서 하나의 사각형은 비스무스(Bi) 원자 4개를 꼭지점으로 하는 원자 격자를 의미하며, 한 변의 길이는 약 0.4 나노 미터(nm; 10억분의 1미터=10⁻⁹m)에 해당함.

Direct observation of ferroelectric field effect and vacancy-controlled screening at the BiFeO₃/La_xSr_{1-x}MnO₃ interface

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The development of interface-based magnetoelectric devices necessitates an understanding of polarization-mediated electronic phenomena and associated polarization screening mechanisms. In this work, the LSMO/BFO interface is studied on a single unit-cell level through a combination of direct order parameter mapping by scanning transmission electron microscopy and electron energy-loss spectroscopy. We demonstrate an unexpected $\sim 50\%$ lattice expansion for regions with negative polarization charge, with a concurrent anomalous decrease of the Mo valence and change in oxygen K-edge intensity. We interpret this behaviour as direct evidence for screening by oxygen vacancies. The vacancies are preferentially accumulated at the narrow oxygen layer of BFO, reflecting the differences of local conductivity between the components. This oxygen exclusion from the interface leads to the formation of a half-unit-cell domain wall. At the same time, purely electronic screening is realized for positive polarization charge, with significant changes in lattice and electronic properties. These results underline the non-trivial role of electrochemical phenomena in determining the functional properties of oxide interfaces. Furthermore, these behaviours suggest that vacancy dynamics and oxidation play major roles in determining interface functionality in oxide multilayers, providing clear implications for novel functionalities in potential electronic devices.

Ferroelectric polarization control of the magnetic properties and metal-insulator transitions in strongly correlated oxides has been an active research goal for the past two decades^{1–3}. This interest stems from applications including new classes of magnetoelectrics and quantum devices. At the same time, these systems offer a platform for exploring the charge-controlled phases of transition metal oxides⁴. Their realizations have stimulated extensive efforts in the development of novel materials and heterostructures^{5–7}.

The development of interface-based magnetoelectric devices requires a understanding of the atomic mechanisms responsible for the coupling between polarization, electronic and spin ordering⁸. Given the important role of charge screening phenomena on the interfacial ferroelectricity of heterostructures, such studies must also address long-standing issues such as the stability of the ferroelectric state in nanoscale systems and the ferroelectric size effect. In addition to purely physical mechanisms, a number of recent studies have suggested that the redistribution of oxygen molecules can play a significant role in oxide interfaces, modulating their electrochemical degree of freedom to be taken into account^{9–11}. Despite such efforts, direct observation of screening phenomena at the interface remains elusive, and the mechanism and state of vacancies remain unexplained. It is thus necessary to design and the interplay between vacancy and electronic redistribution are revealed by the nature of the material. Hence, non-trivial behaviour can be expected depending on vacancy-resonance polarization localization,

with the simplest examples of such an effect being the dipole moment density localizations and work functions at the interfaces.

The recent successes of aberration-controlled (scanning) transmission electron microscopy¹² has enabled atom-level observation of polarization domains in ferroelectric domain walls¹³ and interfaces^{14,15}, as well as structural¹⁶ and topological effects^{17,18}. Here, we report observations of the electronic and electrochemical effects induced by ferroelectric polarization using combined polarization mapping and electron energy-loss spectroscopy. Direct observation of the lattice size change of a matter atom provides evidence for the ferroelectric field effect in oxide heterostructures. This behaviour is further correlated with lattice expansion, protonation and electronic phenomena on the interfacial polarization-dependent properties of oxide interfaces and clearly differentiating the non-trivial effect induced by oxygen molecules.

As a model system, we have chosen the BiFeO₃/La_xSr_{1-x}MnO₃ interface (BFO/LSMO). Previously, it was shown that the interfacial structure of BFO can change markedly depending on the oxygen stoichiometry and polarization direction¹⁹. Here, we present direct observation of the interfacial structure of the prepared BFO revealed the presence of multiple interfacial domains, and therefore multiple domain boundaries. Atomic-resolution studies of such boundaries as a zero-magnon geometry can distinguish contributions to interface structure related to polarization orientation and polarization charge from those related to stress, crystalline tilt and other polarization-induced interface features.

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[그림 2] 관련 논문