

First-principle study of resistance switching in rutile TiO_2 with oxygen vacancy

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With quickly approaching the scaling limit of flash memory, the interest in alternative non-volatile memory (NVM) technologies has been significantly increased. One of the candidates for the next generation non-volatile memories is the Resistive Random Access Memory (ReRAM). ReRAM is very promising for advanced NVMs technologies in terms of low operating power, high density, better non-volatility, fast switching speed, and compatibility with conventional CMOS process. The structure is composed of a resistance changeable material sandwiched by two terminal electrodes. Resistance change can be achieved by controlling the current or voltage pulse applied to the electrodes, and the resistance state remains stable without being refreshed.

Up to date, a number of different switching characteristics have been established in variety of material systems. In fact, it has become well understood that a number of combinations of an oxide with metal electrodes can exhibit some kinds of resistance switching behavior, i.e. typical materials like perovskite or binary transition metal oxides. So far several switching models have been proposed; i.e. charge trapping model, conductive filament model, Mott transition, schottky barrier model, and electrochemical migration of point defects. However, none of these models can explain the switching phenomenon totally due to the lack of fundamental understanding of the undergoing resistance switching process. In order to elucidate the operating principles accurately, in-depth understanding of the resistance switching mechanism at the atomistic level is necessary: i.e. how the conducting paths are formed and disconnected. It is difficult to find the answers to the above question purely from experimental results, therefore, we present a theoretical approach that involves first principles calculations based on density functional theory (DFT). Our study is focused on the impact of oxygen vacancies on the electronic structure of TiO_2 investigating if vacancies in this transition metal oxide can give rise to the generation of charge carriers or conducting channels.

In this study, first principles calculations employing the local density approximation (LDA) and generalized gradient approximation (GGA) with Hubbard-U (on-site Coulomb) corrections have been used for the study of rutile TiO_2 . The conduction band states are dominated by the Ti 3d orbitals, while the valence band states are mainly composed of O 2p orbitals hybridized with Ti 3d orbitals. So far the electronic structure study of this material had been limited by the lack of a proper exchange and correlation approximation that is critical for the study of band gap states. Here we show that the electronic structure of TiO_2 is strongly affected by the on-site Coulomb interaction between electrons and propose a method that can be used to obtain accurate results. Very good agreement is found with the experimental band gap results, when an optimum Hubbard-U is chosen. We find that the position of the band gap state induced by the oxygen vacancy is also strongly affected by the on-site Coulomb interactions. We present a comprehensive discussion of the local structural modifications, vacancy creation energy and electronic structure of the vacancies in a supercell of rutile TiO_2 .