Density-functional-theory Study of Monatomic and Diatomic Vacancies on the Non-polar ZnO(10\bar{1}0) Surface

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We report density-functional-theory calculations on vacancies on the ZnO(10\bar{1}0) surface with the on-site Coulomb interaction correction. Zn and O vacancies and three different configurations of ZnO divacancies were examined considering all the possible charge states. Using the calculated vacancy formation energies, we constructed the phase diagram by spanning the allowed range of electronic and ionic chemical potential. Differently from the bulk where the divacancy is not stabilized at all, one configuration of surface divacancies can be stable in a certain region of the chemical potentials. Among all the stable vacancies, only the neutral and the singly negatively-charged monatomic Zn vacancies exhibit a finite magnetic moment of \(1\ \mu_B\), which implies that the surface Zn vacancies may be responsible for the experimentally-observed room-temperature ferromagnetism in ZnO nanocrystals.

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I. INTRODUCTION

Recently, nonmagnetic metal oxides have emerged as candidate spintronic materials due to the observation of room-temperature (RT) ferromagnetism (FM) in HfO\(_2\), TiO\(_2\), and ZnO without doping of magnetic ions [1,2]. Because these metal oxides do not have any unpaired electrons, the observation of FM has triggered many studies to find its origin. Among these metal oxides, ZnO is of particular interest because it is a semiconductor with a wide band gap of \(\sim 3.4\) eV and with a large exciton binding energy of \(\sim 60\) meV [3].

Sundaresan and Rao attributed the FM to an exchange interaction of O vacancies \(V_O\) located at the surfaces of nanoparticles [2]. Wang et al. proposed that the Zn vacancy \(V_{Zn}\) preferred to reside on the surfaces of thin films and nanowires with a finite magnetic moment [4]. Theoretically, the bulk Zn vacancy \(V_{Zn}\) has been proposed as an important candidate for the FM due to the unpaired \(p\) electrons at the dangling bonds of nearest-neighbor (NN) O ions to \(V_{Zn}\) [5,6]. However, this proposition was opposed by the energetic stability of monatomic vacancies. For instance, the O vacancy \(V_O\) is more stable than \(V_{Zn}\) over a wide range of electronic and atomic chemical potentials [7,8]. On the other hand, a negatively-charged \(V_{Zn}\), known to be an electron trap, is found to be more stable than neutral vacancies, but to have a reduced magnetic moment [8,9]. The charged \(V_{Zn}\) was experimentally observed [10] and was considered to be a potential origin of the RT-FM. In a recent paper, we performed an extensive set of first-principles calculations on the monatomic and diatomic vacancies in bulk ZnO by taking into account the possible charge states, and we found that the bulk vacancies could not be the origin of the FM [11].

The shape of a nano-sized crystal is decided by the surface energies of different low-index surfaces. The low-index surfaces of the hexagonal ZnO are the (0001) and the (000\bar{1}) polar surfaces, the (10\bar{1}1) and the (\bar{1}01\bar{1}) semipolar surfaces, and the non-polar (10\bar{1}0) and (11\bar{2}0) surfaces. Zn-terminated (0001) and O-terminated (000\bar{1}) surfaces are important because they are commonly used for thin-film growth. However, if the energetic stability is considered, the non-polar (10\bar{1}0) surface is more stable than the polar surfaces [12]. This causes ZnO nanowires to have a hexagonal cross section [13] and the (10\bar{1}0) facet to be the largest. One of the authors reported that the neutral \(V_{Zn}\) could carry a finite magnetic moment on two non-polar surfaces of ZnO, 1 \(\mu_B\) for (10\bar{1}0) [14, 15] and 2 \(\mu_B\) for (11\bar{2}0) [16], while \(V_O\) is non-magnetic.

In this paper, we report a comprehensive set of first-principle calculations on Zn and O monatomic vacancies and the ZnO diatomic vacancy (DV) on the most stable ZnO(10\bar{1}0) surface. We investigate the energetic stabilities of the vacancies by taking into account various possible charge states. For each vacancy, stable charge states are identified, and their electronic structures are addressed by using the atom-projected density of states

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II. COMPUTATIONAL METHOD

We have performed first-principles calculations based on density functional theory (DFT) by using the Vienna Ab initio Simulation Package (VASP) [17]. We used a plane-wave basis set with a kinetic energy cutoff of 450 eV. The ions were represented by projector-augmented-wave (PAW) potentials [18], and the exchange-correlation interaction was described within the generalized gradient approximation (GGA) by employing the Perdew-Burke-Ernzenhof (PBE) functional [19]. As the GGA seriously underestimates the band gap of ZnO compared with the experimental value, we used the DFT+U scheme by including the on-site Coulomb repulsion parameter \( U = 6 \) eV) [20], which corrected the band gap from 0.7 eV to 2.0 eV.

To model the surface vacancies, we used the theoretical equilibrium lattice constants \( (a = 3.18 \) Å and \( c = 5.12 \) Å), which are in good agreement with the experimental values [21]. We employed a \( 4 \times 3 \) surface supercell, a four-bilayer slab, and a 12-Å-thick vacuum layer. The bottom surface of the slab was passivated with fictitious H atoms. The \( k \)-point sampling was done by using a \( 2 \times 2 \) \( \Gamma \)-centered Monkhorst-Pack-type grid [22]. The atomic geometries were fully optimized by requiring the Hellmann-Feynman forces to be smaller than 0.01 eV/Å.

The formation energy of a surface vacancy with the charge state \( q \), \( E_{\text{form}}(q) \), was calculated by using

\[
E_{\text{form}}(q) = E_{\text{tot}}^{\text{defect}}(q) - E_{\text{tot}}^{\text{clean}} + \sum_i n_i \mu_i + q(E_F + E_{\text{VBM}}),
\]

where \( E_{\text{tot}}^{\text{defect}}(q) \) is the total energy of a slab with a charged defect, \( E_{\text{tot}}^{\text{clean}} \) is the total energy of a clean slab, \( E_F \) is the Fermi level referenced to the valence-band maximum \( (E_{\text{VBM}}) \), and \( \mu_i \) \((i=Zn, O)\) are the atomic chemical potentials. If thermodynamic equilibrium \( (\mu_{Zn} + \mu_O = \mu_{ZnO}^{\text{bulk}}) \) is assumed, the Zn and the O chemical potentials are not independent, and the allowed range of \( \mu_{Zn} \) is

\[
\Delta H_f \leq \mu_{Zn} - \mu_{Zn}^{\text{bulk}} \leq 0,
\]

where \( \Delta H_f \) is the formation enthalpy defined by \( \Delta H_f = \mu_{ZnO}^{\text{bulk}} - \mu_{Zn}^{\text{bulk}} - \frac{1}{2} \mu_{O}^{\text{gas}} \). From our DFT+U calculations, \( \Delta H_f \) was obtained to be \(-3.4 \) eV, which is in agreement with the experimental value, \(-3.6 \) eV [21]. Under a Zn-rich condition, \( \mu_{Zn} = \mu_{Zn}^{\text{bulk}} \) \( (\mu_O = \frac{1}{2} \mu_{O}^{\text{gas}} + \Delta H_f) \), and under an O-rich condition, \( \mu_{Zn} = \mu_{Zn}^{\text{bulk}} + \Delta H_f \) \( (\mu_O = \frac{1}{2} \mu_{O}^{\text{gas}}) \).

III. RESULTS AND DISCUSSION

The creation of monatomic surface vacancies is straightforward, but DVs can be formed in three different configurations on the \( (1010) \) surface as shown in Fig. 1. The ZnO bonds in ZnO are divided into two kinds depending on their direction. One is along the wurtzite armchair chain direction, which is parallel with the hexagonal \( c \)-axis, and the other is along the zigzag chain direction \((a \)-axis\). We will call the DV as \( DV_A \) and \( DV_Z \) if a Zn-O pair is removed from a ZnO bond directed along the armchair and the zigzag chain, respectively. In \( DV_A \), two atoms are removed from the surface. However, in \( DV_Z \), one of the two atoms is removed from the surface and the other is removed from the subsurface. Therefore, two different configurations are possible for \( DV_Z \). If the surface Zn (O) atom is removed, then the resulting DV will be named as \( DV_{Zn,Zn} \) \((DV_{Z,O}) \).

The calculated formation energies of the five vacancies \( (V_{Zn}, V_{O}, DV_A, DV_{Z,O}, DV_{Z,Zn}) \) in their possible charge states are summarized in Table 1, and are compared with those of the bulk vacancies. According to our previous calculations [11], DVs are less stable than monatomic vacancies in the bulk throughout the entire ranges of the electronic and the ionic chemical potentials. In stark contrast to the bulk case, surface DVs can be energetically favored to the surface \( V_{Zn} \) and \( V_{O} \) for certain ranges of electronic and ionic chemical potentials. This is attributed to the fact that one has to break six bonds to create a bulk DV while the surface DV requires fewer broken bonds (four and five for \( DV_A \) and \( DV_Z \), respectively). This also explains the reason the surface \( DV_A \) is more stable than the surface \( DV_Z \) by \( \sim 1.7 \) eV.

In order to provide a more comprehensive view for the energetic stability of surface vacancies, we have plotted a phase diagram in Fig. 2. This phase diagram indicates the region of electronic and ionic chemical potentials where each vacancy with a specific charge state is