Shallow Donor States Induced by In-Diffused Cu in ZnO: A Combined HREELS and Hybrid DFT Study

Hengshan Qiu,[1] Federico Gallino,[2] Cristiana Di Valentin,[2,*] and Yuemin Wang[1,†]

[1]*Department of Physical Chemistry I and Laboratory of Industrial Chemistry, Ruhr University Bochum, D-44780 Bochum, Germany*

[2]*Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, 20125 Milano, Italy*

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A combined experimental and first principles study of Cu defects in bulk ZnO is presented. Cu particles are epitaxially deposited on the polar O-ZnO($000\bar{1}$) surface at room temperature. Upon heating, a broadening of the quasielastic peak in high resolution electron energy loss spectra is observed, corresponding to an electronic doping effect of Cu atoms in bulk ZnO with an ionization energy of 88 meV. Cu impurities in ZnO, although commonly acting as acceptors, are presently observed to induce shallow donor states. We assign these to interstitial Cu species on the basis of a hybrid density functional study.

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Zinc oxide is a wide band-gap semiconductor that has been recently attracting an increasing interest in the scientific community, especially for its promising applications in optoelectronics, spintronics, and catalysis [1–3]. In particular, the perspective of preparing a material combining both magnetic and semiconducting properties has prompted an intense research activity aimed at identifying a valuable and reliable transition metal dopant, in a so-called diluted magnetic semiconducting oxide with room temperature (RT) ferromagnetic properties [4–10]. Elements like Mn and Cu, that do not present secondary ferromagnetic phases due to partial clustering, are highly preferred. In addition, the Cu/ZnO system has been largely used as an excellent catalyst for the industrial methanol synthesis. However, key questions on the microscopic mechanism of the reaction are still open and the incorporation of Cu atoms into ZnO may play a role in determining the catalytic activity of Cu/ZnO [11,12].

Cu doping of ZnO has been previously achieved by either pulsed-laser ablation or high temperature diffusion ($>1000\,^{\circ}$C), resulting in Cu ions substituting lattice Zn ions [10,13]. Several studies based on photoluminescence experiments [14,15], electrical measurements [16,17], and on GGA + U calculations [18] have reported a deep acceptor state with the transition energy level $(0, -1)$ high in the band gap. In this Letter we present a combined experimental and theoretical study of the Cu/ZnO system prepared by Cu deposition on ZnO single crystal surfaces. The high resolution electron energy loss spectroscopy (HREELS) data reveal that Cu can diffuse into bulk ZnO by a mild thermal treatment yielding an unusual donor state in ZnO. Theoretical modeling suggests that the shallow donor state results from the formation of interstitial Cu^{+} ions in ZnO.

All experiments were carried out in a HREELS system, as described in a previous work [19]. In short, the ZnO($000\bar{1}$) sample was prepared by repeated cycles of Ar ion sputtering and subsequent annealing at 850 K for 10 min. The Cu evaporator used in this work is a homemade setup with an electronic beam heating. The film thickness is measured by a quartz crystal with an experimental error of about 10%. The broadening (Δ) of the quasielastic peak in HREELS is derived according to the formula $\Delta_{\mathrm{tot}}^2 = \Delta_{\mathrm{app}}^2 + \Delta^2$ [19], where Δ_{app} denotes the apparatus broadening.

The calculations have been performed within spin-polarized density-functional theory (DFT), using the hybrid B3LYP functional [20]. The Kohn–Sham orbitals were expanded in Gaussian type orbitals, as implemented in CRYSTAL06 package [21] [the all-electron basis sets are O 8-411(d1) [22], Zn 8-64111(d411) [23] and Cu 8-6411(d41) [24]]. The bulk wurtzite ZnO has been modeled by a 192-atoms supercell $[4 \times 4 \times 3]$ with optimized bulk lattice parameters: $a = 3.278$ Å, $c = 5.287$ Å. The reciprocal space was sampled in a $2 \times 2 \times 2$ k-point mesh. We refer to a previous work for the detailed description of the theoretical approach to compute formation energies (E_{form}) and transition energy levels (ε) [25,26]. Thermodynamic transition levels ($\varepsilon^{\mathrm{therm}}$) of defects in bulk materials can be directly compared to donor levels ionization energies, as determined with the experimental approach of this and previous work [19].

The polar O-ZnO($000\bar{1}$) surface is electrostatically unstable because of uncompensated surface charges and exhibits a complex surface structure [3]. The HREEL spectrum of the clean O-ZnO surface is characterized by intense Fuchs-Kliewer phonons at 68, 135 and 201 meV (see Fig. 1) [27]. After deposition of Cu up to 20 monolayers (ML) at RT, the surface phonons are fully screened by Cu layer. They reappear and increase in intensity with annealing the sample to higher temperatures. Upon heating to 825 K, the spectrum of Cu/O-ZnO becomes comparable with that of the clean O-ZnO (Fig. 1). We can first rule out the possibility of Cu desorption from the surface, as confirmed by the corresponding thermal desorption spectroscopy data (not shown). The present HREELS results could

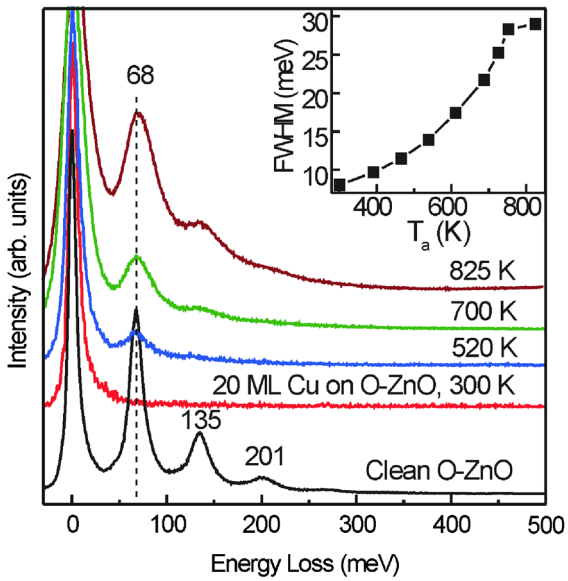

FIG. 1 (color online). HREEL spectra obtained after 20 ML Cu deposition on the clean O-ZnO(000$\bar{1}$) surface at 300 K and then annealing to the indicated temperatures. The inset shows the FWHM value of the quasielastic peak as a function of annealing temperature T_a. All spectra were recorded at room temperature in specular geometry with the primary electron energy of 10 eV and incident angle of 55° with respect to the surface normal.

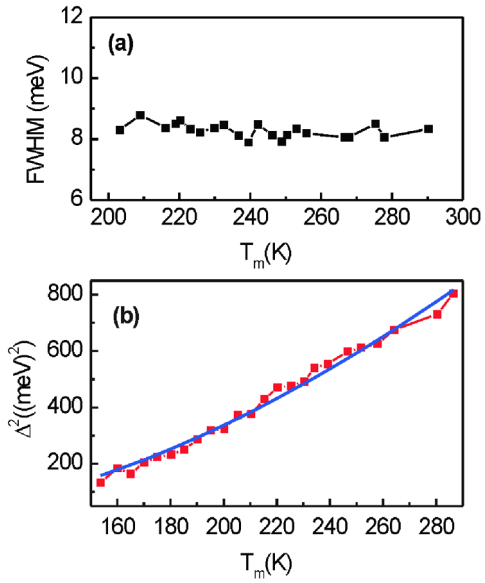

FIG. 2 (color online). (a) The broadening (FWHM, Δ) of the quasielastic peak in HREELS as a function of the measurement temperature T_m for the clean O-ZnO(000$\bar{1}$) surface deposited with 20 ML of Cu at 120 K without further heating treatment. (b) The value of Δ^2 as a function of the measurement temperature T_m for the Cu/O-ZnO sample prepared by 20 ML Cu deposition at RT followed by annealing to 825 K and then cooling down to 120 K. The solid curve in (b) is the result of a nonlinear least squares fit, which gives an ionization energy of 88 meV.

be attributed to the aggregation of Cu particles on ZnO(000$\bar{1}$) and/or diffusion into bulk ZnO. Importantly, the reappearance of the Fuchs-Kliewer phonons is accompanied by a dramatic increase of the full width at half maximum (FWHM) value of the quasielastic peak in HREELS (see inset of Fig. 1). Obviously, this significant peak broadening cannot be explained by the aggregation of Cu clusters on O-ZnO, but, according to similar observations on H/O-ZnO [19], it originates from the excitation of low-energy plasmons, which is related to an electronic doping effect of Cu defects formed via diffusion into bulk ZnO. This assignment is further evidenced by additional experiments discussed below.

For doped semiconductors, the broadening (Δ) of the quasielastic signal in HREELS depends on the density of free charge carriers and the sample temperature [28]. For comparison, we carried out temperature-dependent experiments on differently treated Cu/O-ZnO samples. Figure 2 presents the results of Δ (Δ^2) as a function of temperature below 300 K. For the sample freshly prepared by deposition of 20 ML Cu at 120 K without additional heating treatment, the FWHM is nearly constant with a slight deviation within the experimental error, indicating no formation of shallow donor states, thus confirming that Cu atoms do not diffuse into bulk ZnO below RT. In contrast, for the Cu/O-ZnO sample obtained after first annealing to 825 K and then cooling down to low temperatures, the value of Δ^2 exhibits a continuous increase with raising the measurement temperature T_m [Fig. 2(b)]. This finding provides another experimental evidence for the electronic doping effect of Cu species incorporated in bulk ZnO.

On the basis of the formula for temperature-dependent conduction band (CB) charge density n and the broadening Δ as described in [19], we can further estimate the corresponding ionization energy. The solid curve in Fig. 2(b) presents the result of Δ^2 as a function of temperature calculated by a nonlinear least square fit, yielding an ionization energy of 88 meV. This rather small value corresponds to the formation of shallow donor states created by the incorporation of Cu atoms in bulk ZnO, which is not simple to rationalize since all Cu related species in ZnO have been reported in the literature as deep acceptors with ionization energies larger than 2 eV [14–17]. Note that a deep acceptor state would not lead to an apparent quasielastic peak broadening in HREELS. In order to understand the origin of the low ionization state, we have carried out a DFT investigation by means of the hybrid density functional B3LYP, which reproduces with excellent accuracy the bulk ZnO band gap (experimental 3.44 eV [29] vs theoretical 3.38 eV).

Copper doping of ZnO is commonly viewed as Cu substitution of one lattice Zn^{2+} ion (Cu_s). This results in the presence of a hole in the Cu 3d shell (Cu_s^{2+}), which causes a Jahn-Teller distortion of the tetrahedral coordination sphere with formation of a short Cu-O distance

(from 2.00 to 1.90 Å) along the c axis. The unpaired electron is highly localized on a Cu d_{z^2}-orbital. The Cu_s^{2+} species has been previously studied and identified as a deep acceptor [18,30,31]. The addition of an extra electron fills up the Cu $3d$ shell (Cu_s^{+}) and induces a considerable outward relaxation of the nearest O atoms ($E_{rel} = 0.58$ eV), restoring the original zinc tetrahedral coordination. Further addition of a second extra electron does not cause significant distortion of the system but only a tiny distortion of the bottom of CB in a commonly described perturbed host state (PHS) [32], where the electron is delocalized. The corresponding $(0/-1)$ and $(-1/-2)$ transition energy levels computed with the present computational setup (0.91 and 0.12 eV below the CB bottom, respectively) are consistent with the experimental data and a recent GGA + U study [18]. While Cu_s^{2+} is a good acceptor that can easily capture electrons from any shallow donors present in the bulk [$(0/-1)$ charge transition], Cu_s^{+} is a very poor acceptor [$(-1/-2)$ charge transition]. Concluding, a stoichiometric excess of donors with respect to Cu_s^{2+} acceptor species can result in a residual n-type conductivity.

The question is the following: which type of donors could be present? A generally recognized double electron shallow donor is interstitial zinc (Zn_i) in ZnO. Since Cu_s is a single electron compensating acceptor, if one Cu atom kicks out one Zn atom from its lattice position, forming a Cu_s and a Zn_i species, we expect an extra electron stabilized at the CB bottom which could be responsible of a n-type conductivity. Thus, we investigated the copresence of these defects (Cu_sZn_i) in a nearby (2.4 Å) or far apart (10.0 Å) configuration. The Cu_s and Zn_i species prefer to be in close contact (by 1.5 eV) as a consequence of a significant lattice rearrangement. Cu and Zn atoms share the same lattice site in a so-called split-interstitial configuration (see Fig. 3). The electronic structure of the system is very similar to that observed for Cu_s^{+}. This indicates that only the first electron from the Zn impurity has been transferred to the Cu_s while the second lies in a PHS. The system is a shallow donor with thermodynamic transition level $\varepsilon^{therm}(+1/0)$ computed to be 113 meV from the CB minimum (see Fig. 4).

Cu atoms may also occupy interstitial voids in ZnO (Cu_i). Since for Zn_i the octahedral cavity was found to be 0.9 eV more stable [33], we assume a similar situation for Cu_i (see Fig. 3). Similar structural relaxations are observed for Cu_i and Zn_i, with almost identical distances to O (2.07 Å [25]) and to the nearest Zn ions (2.44–2.59 Å [25], 2.42–2.50 Å, respectively). Differently from Zn_i, a double electron shallow donor, Cu_i is expected to behave as a single electron shallow donor, which is confirmed by the present calculations. The thermodynamic transition level $\varepsilon^{therm}(+1/0)$ for Cu_i defect center is computed to be 126 meV from CB minimum which is, as for the case of Cu_sZn_i (113 meV), in rather good agreement with the experimentally determined 88 meV (see Fig. 4).

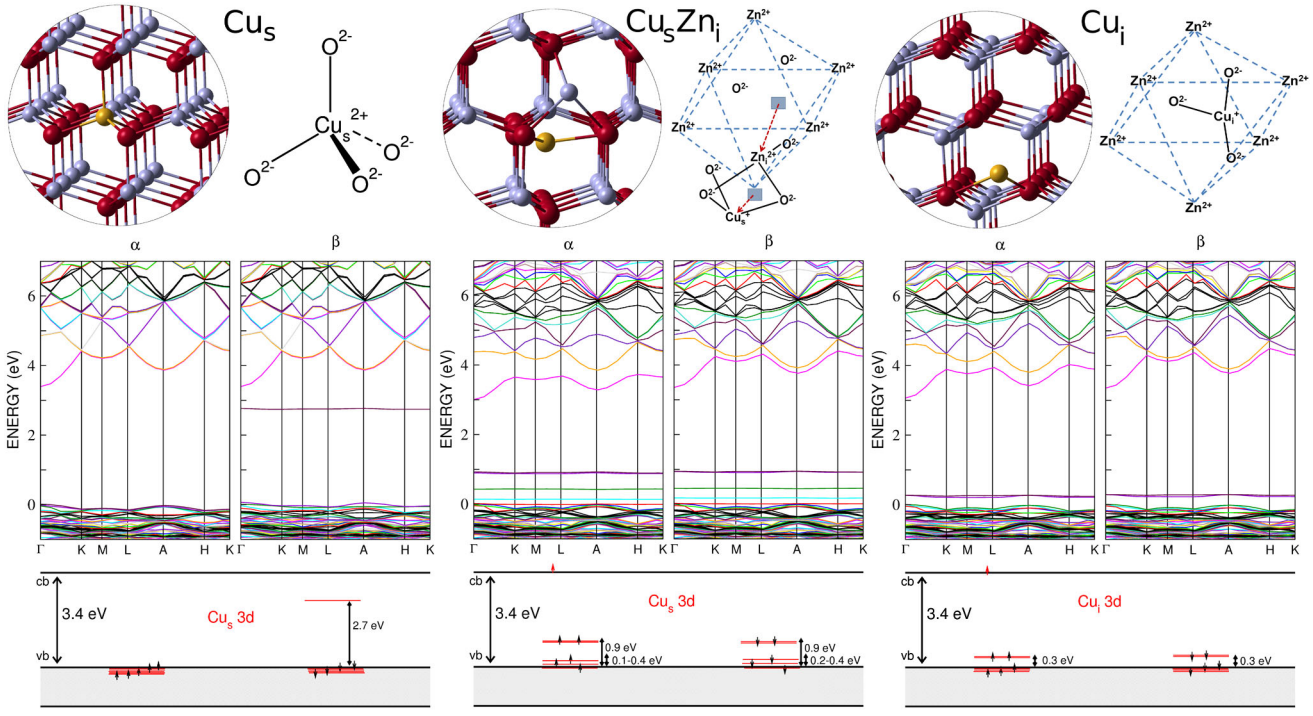

FIG. 3 (color online). Upper panel: ball and stick and schematic representations of the Cu species in bulk ZnO. Zn, O, and Cu are represented by small light gray, large dark (red), and medium size gray (yellow) spheres, respectively. Lower panel: band structures for the various models together with a schematic representation of the Cu d states in the band gap of the material (from Kohn-Sham eigenvalues). The highest (red) arrow for Cu_sZn_i and Cu_i represents the unpaired electron delocalized in the CB.

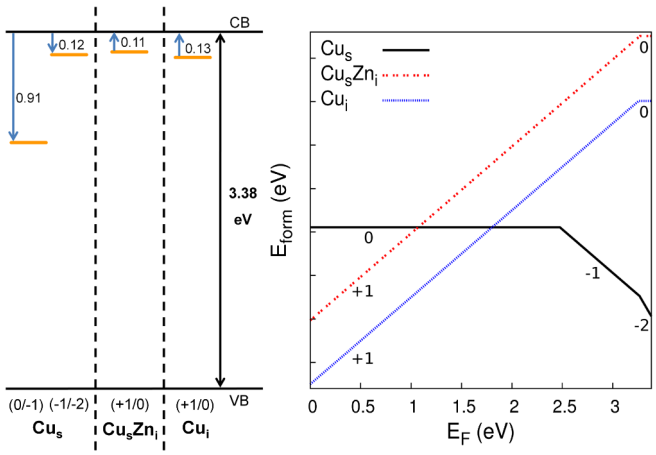

FIG. 4 (color online). Left panel: thermodynamic transition levels (eV) in the band gap of ZnO for Cu acceptor (↓) and donor (↑) species in bulk ZnO. Right panel: formation energy of Cu defects as a function of the Fermi level at the oxygen-poor limit. The slope corresponds to the charge state of the defect considered. Tick marks unit on the y axis is 0.5 eV.

We have identified one deep acceptor (Cu_s) and two shallow donor species (Cu_sZn_i and Cu_i) with computed donor ionization energies in good agreement with the experimental value. The stability of these species is now compared at the oxygen-poor limit (further details are in Ref. [34]). Formation energies are reported as a function of the Fermi level (E_F) ranging from the top of the VB to the bottom of the CB. While absolute values of formation energies are dependent on the choice of reference compounds, relative values are not. We observe that the Cu_sZn_i species is always less stable than the Cu_i species by 0.75 eV. The most stable species at low Fermi level values ($E_F < 1.80$ eV) is Cu_i (in particular Cu_i^+), while at high Fermi level values ($E_F > 1.80$ eV) it is Cu_s. These results mean that Cu_i is always a better donor species than Cu_sZn_i and is the predominant defect for a broad range of E_F. Only for an electron rich system, which is not the present case, an acceptor species such as Cu_s becomes favored.

In conclusion, the present HREELS data demonstrate that Cu particles deposited on the O-ZnO($000\bar{1}$) surface can diffuse into bulk ZnO by thermal treatment at temperature higher than RT. Cu, commonly reported as an acceptor species in bulk ZnO, is presently found to induce a shallow donor state, leading to a dramatic quasielastic peak broadening in the HREEL spectra. A temperature-dependent analysis of the broadening gives an ionization energy of 88 meV. Based on the very good agreement of this value with the computed thermodynamic transition energy levels from a hybrid density functional investigation, we propose the shallow donor species to be interstitial Cu in bulk ZnO.

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*cristiana.divalentin@mater.unimib.it
†wang@pc.rub.de

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