

Ionization Energies of Shallow Donor States in ZnO Created by Reversible Formation and Depletion of H Interstitials

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The electronic effects of H atoms at interstitial sites in ZnO have been investigated by high resolution electron energy loss spectroscopy (HREELS). A reversible doping is achieved by exposing single crystalline (000 $\bar{1}$)-oriented ZnO substrates to atomic hydrogen. At low temperatures, interstitial H atoms form shallow donor states. At sufficiently high temperatures, the electrons are excited into the conduction band. We use EELS to demonstrate the presence of plasmons resulting from this finite density of charge carriers in the conduction band. Above temperatures of 100 K, a strong, plasmon-induced broadening of the quasielastic peak in the HREELS data is observed. The analysis of the temperature dependence yields a donor level ionization energy of 25 ± 5 meV.

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Zinc oxide exhibits a number of extraordinary properties and is one of the most technologically important metal oxides. As a wide band gap semiconductor exhibiting the largest charge-carrier mobility among oxides, it is used in conventional and novel electronic devices, as well as for the construction of UV laser diodes [1]. Undoped ZnO exhibits *n*-conduction properties, a fact that—despite numerous experimental and theoretical studies [2–6]—is still not thoroughly understood. It has long been known that the incorporation of H atoms in the bulk increases the electrical conductivity of ZnO. In fact, ZnO can be used as a detector for hydrogen atoms [7–10]. From the temperature dependence of the electrical conductivity, it is thought that the incorporation of H atoms at interstitial sites gives rise to shallow donor states with an ionization energy of 51 meV [11]. This value, however, is not consistent with donor activation energies of 35 ± 5 meV as obtained from electron paramagnetic resonance (EPR) spectroscopy [4]. It has been proposed that the electrical conductivity experiments are affected by other bulk defects such as oxygen vacancies, which can also interact with H atoms and may have different effects.

The *n*-doping properties of H in ZnO have been corroborated by recent theoretical work [2], where it was proposed that interstitial H atoms always act as donors in ZnO. A reliable value for the ionization (or exciton binding) energy, however, could not be obtained from these calculations.

To enhance understanding of the electronic structure changes induced by H atom interstitials in ZnO, it would be highly desirable to reversibly load and deplete a perfect ZnO single crystal with H interstitials and to directly study the related changes in electronic structure, particularly the presence of electrons in the conduction band (CB). To this end, we have carried out a systematic investigation of ZnO

single crystals exposed to hydrogen atoms by high resolution electron energy loss spectroscopy (HREELS). We observe electronic excitations in the meV regime and assign them to plasmon losses resulting from the occupation of CB states.

The experiments were carried out in an UHV apparatus with a base pressure better than 5×10^{-11} mbar, equipped with an HREEL spectrometer [12], LEED optics, and a mass spectrometer [13,14]. The O-terminated ZnO(000 $\bar{1}$) surface (O-ZnO) was prepared using sputtering and annealing cycles as described previously [15,16]. The LEED pattern recorded for the clean O-ZnO surface exhibited (1×3) superstructure spots, as reported previously [17]. This clean, reconstructed (1×3) O-ZnO surface is very reactive towards H₂O adsorption and quickly converts into a very stable, structurally well-defined, OH-terminated surface exhibiting a (1×1) LEED pattern termed HO-ZnO [15–17]. Exposure to atomic hydrogen was performed by dissociating H₂ on a hot tungsten filament situated in the line of sight from the substrate. H₂O was dosed on the ZnO surface by backfilling the UHV vessel with water vapor. In the following, exposures will be given in units of langmuirs (L), with $1 \text{ L} = 1.33 \times 10^{-6}$ mbar.s. The width of the quasielastic signal in the EELS data Δ_{app} showed a small day-to-day variation. For the analysis of the data, the most recent value of Δ_{app} was used.

The EELS data for the clean (1×3) O-ZnO surface shown in Fig. 1, curve A, are dominated by intense Fuchs-Kliwer phonon losses (fundamental and multiples) located at 68, 135, 203, and 269 meV [18–20]. For the HO-ZnO substrate, a new loss arising from the OH stretching vibration of the surface hydroxyl species is seen at 449 meV (3621 cm^{-1}), shown in Fig. 1, curve B, a frequency which is close to the value of 3670 cm^{-1} reported for OH species on the mixed-terminated ZnO(10 $\bar{1}$ 0) sur-

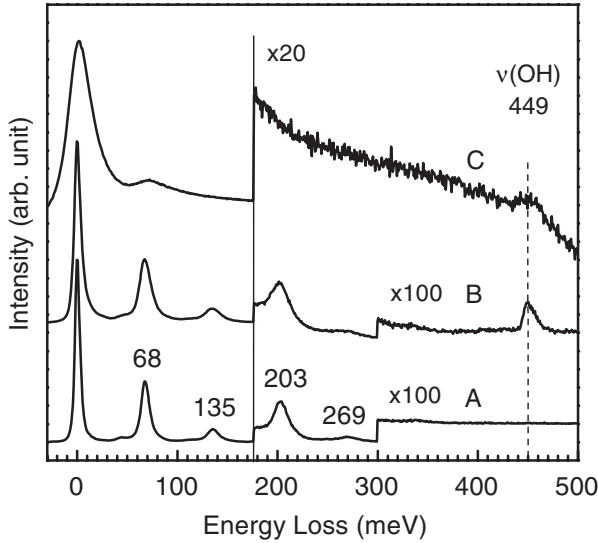


FIG. 1. HREEL spectra of *A* a clean ZnO(000 $\bar{1}$) surface, *B* the HO-ZnO surface prepared by exposure of the clean surface to 2 L H₂O at room temperature, and *C* exposure of the HO-ZnO surface to 1000 L atomic hydrogen at 300 K. All spectra were taken at room temperature in specular geometry with an incidence angle of 55° with respect to the surface normal and with a primary energy of 10 eV.

face [14,21]. The weak feature at 45 meV was also observed in previous works [22,23] and was attributed to a vibrational mode localized at defects.

For the spectrum shown in Fig. 1, curve *B*, recorded for the HO-ZnO surfaces, the full width at half maximum (FWHM, Δ_{tot}) of the quasielastic peak is equal to 6 meV, slightly larger than the FWHM of the resolution of HREELS apparatus (4 meV) as determined in experiments on a clean Pt(111) substrate. Similar broadenings of the quasielastic signal in EELS have been observed for other semiconductors: Si [24,25], GaAs [26], and Ge [27]. In following these previous works, we attribute the broadening of Δ_{tot} seen for ZnO substrates to an interaction of the incident electrons with plasmons in the semiconductor (SC) substrates. Compared to a metal, the carrier density in a SC is quite low, leading to plasmon energies in the meV regime. Persson and Demuth have derived an elegant formula [25] relating the broadening Δ (given by $\Delta_{\text{tot}}^2 = \Delta_{\text{app}}^2 + \Delta^2$) to experimental parameters, the carrier density n_c , and the substrate temperature T :

$$\Delta^2 = \frac{C}{4} \pi^2 \omega_{\text{sp}}^2 \left[\frac{2}{e^{\hbar\omega_{\text{sp}}/k_B T} - 1} + 1 \right] \cos\alpha, \quad (1)$$

with $C = \frac{4}{\pi} \frac{1}{\varepsilon+1} \frac{1}{\cos^2\alpha} \frac{1}{ka_0}$, $\omega_{\text{sp}} = \omega_p / \sqrt{1 + \varepsilon}$, and $\omega_p = \sqrt{n_c e^2 / m^* \varepsilon_0}$, with ε the relative dielectric constant (4.6 for ZnO [28]), k the wave vector of the incident electron, a_0 the Bohr radius, m^* the effective mass of electrons in ZnO (0.19 m_e for ZnO [29]), ε_0 the vacuum dielectric constant, k_B the Boltzmann constant, ω_{sp} and ω_p the surface and

bulk plasmon frequencies, respectively, and α the electron angle of incidence (55°).

From (1), our experimental parameters, and the materials constants for ZnO, we obtain a carrier density of $9 \times 10^{13} \text{ cm}^{-3}$, a reasonably low value for a clean ZnO substrate. Upon exposing the HO-ZnO surface to atomic hydrogen [see Fig. 1, curve *C*], Δ_{tot} strongly increases. No indications of additional individual losses could be detected in the EELS data. In particular, we were unable to detect Zn-H vibrations, which have been observed at around 200 meV (1613 cm^{-1}) on other ZnO surfaces [21]. This is expected, since according to the current structural models for this surface [17] the HO-ZnO surface does not expose the Zn atom. The increase of Δ_{tot} was found to be completely reversible: Heating the ZnO specimen (and thus removing the H atoms) reduced Δ_{tot} to its original value. We did not observe any indication of a band arising from bulk OH stretching vibrations at about 3327 cm^{-1} , which has been detected in IR transmission experiments [30].

A similar broadening upon exposure to atomic H has been reported for the ZnO(10 $\bar{1}$ 0) surface, where the broadening was linked to the formation of a partially filled, H-induced electronic surface state [21]. In the present case, however, the surface is already hydroxylated and fully oxidized prior to H atom exposure. Density-functional theory (DFT) calculations have shown that the surface hydroxylation is the most efficient means to stabilize the polar surface termination of O-ZnO [31].

The complete hydroxylation of the HO-ZnO surface has been demonstrated by a study of CO adsorption on this surface [32] and is further evidenced by the presence of the OH stretching mode and the absence of any other features in the EELS data after H exposure.

The H atoms impinging on the HO-ZnO substrate diffuse into the bulk, forming H interstitials in the subsurface region. Their presence is clearly revealed by thermal desorption spectroscopy (TDS). As shown in Fig. 2(a), after loading the hydroxylated substrate with atomic hydrogen at 300 K, the TDS data reveal an additional H₂ desorption peak ($m/e = 2$) at ~ 500 K. The H₂ peak was not seen for the HO-ZnO surface that was not exposed to H atoms. The desorption of water from the HO-ZnO surface, however, is unaffected by the exposure to H atoms, as seen in Fig. 2(b).

Using (1) we can calculate the carrier density n_c from the broadening Δ and yield a value of $1 \times 10^{17} \text{ cm}^{-3}$. When the HO-ZnO substrate is heated to higher temperatures, the broadening decreases continuously as shown in Fig. 3(a). Figure 3(b) shows $d(\Delta^2)/dT$ as a function of annealing temperature. The curve reveals two peaks at 455 and 515 K. By comparison with the hydrogen TDS results [Fig. 2(a)], the peak at 515 K can be attributed to H₂ desorption from the surface. The maximum observed at 455 K, on the other hand, is not detected in TDS experiments and, accordingly, must be due to diffusion of H

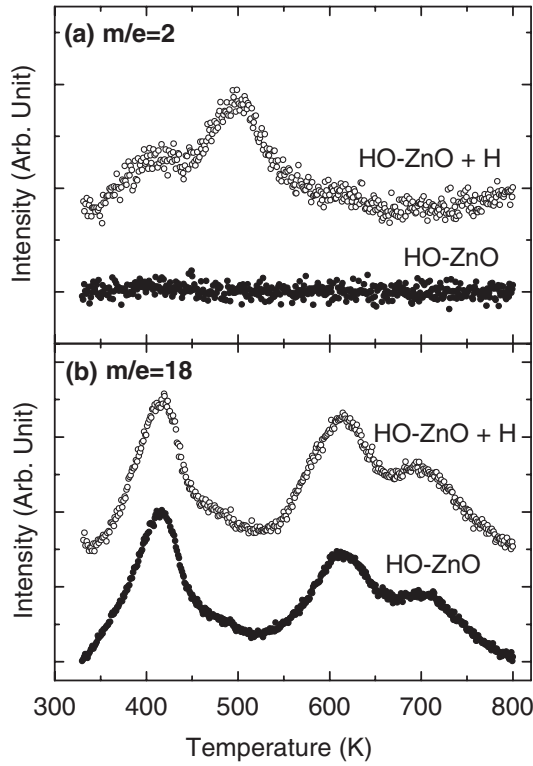


FIG. 2. (a) Thermal desorption spectra for $m/e = 2$, representing H_2 , of the HO-ZnO surface (prepared by exposure to H_2O) before (solid cycles) and after (hollow cycles) exposure to 1000 L atomic H. (b) The same as (a) but for $m/e = 18$, representing water. The heating rate was 1.5 K/s.

atoms into deeper bulk regions. The corresponding diffusion barrier E_{diff} can be estimated from this temperature (455 K) according to

$$\frac{E_{\text{diff}}}{k_B T_{\text{max}}^2} = \frac{\nu}{\beta} \exp\left(\frac{E_{\text{diff}}}{k_B T_{\text{max}}}\right),$$

where ν is a preexponential factor, β is the linear heating rate, and T_{max} is the temperature corresponding to the maximum diffusion rate. This equation is derived from $\frac{dn}{dt} = \beta \frac{dn}{dT} = -\nu n \exp\left(-\frac{E_{\text{diff}}}{k_B T}\right)$ and $\frac{d^2n}{dT^2} = 0$ for the maximum diffusion rate. For a heating rate of $\beta = 1.5 \text{ K s}^{-1}$ and a preexponential factor ν of 10^{13} s^{-1} , an activation energy of 1.26 eV is obtained, in reasonable agreement with the experimental value ($\sim 1.0 \text{ eV}$) reported for H atom diffusion in bulk ZnO [7,8]. For the H_2 desorption peak at 515 K, an activation energy for desorption of 1.44 eV is deduced, which also agrees well with the results of recent DFT calculations [33].

Having provided compelling evidence that the increase of Δ seen in our EELS data results from a finite density of electrons in the conduction band, we next investigate the temperature dependence of Δ below 300 K, where any diffusion of H atom can be safely ruled out.

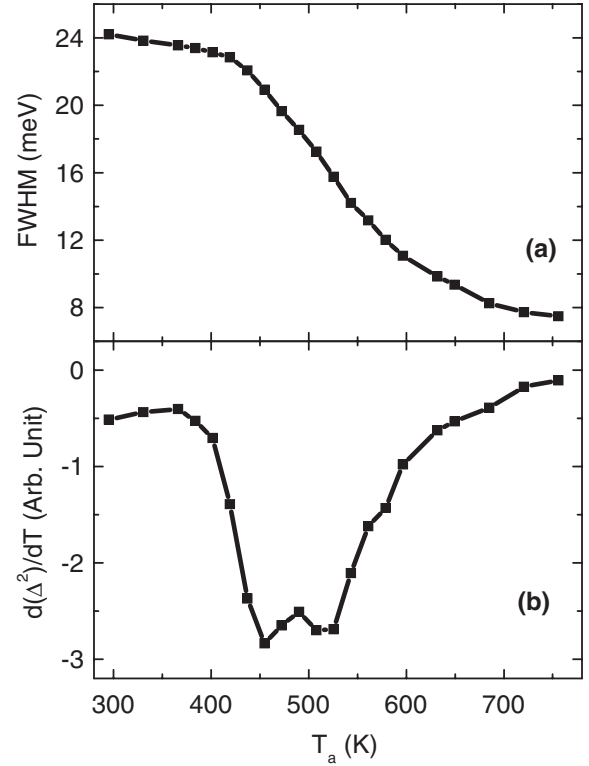


FIG. 3. (a) FWHM of the quasielastic peak Δ in the HREEL spectra (measured at RT) as a function of annealing temperature T_a after exposing the HO-ZnO surface to 1000 L atomic hydrogen at 300 K. (b) $d(\Delta^2)/dT$ as a function of the annealing temperature. Annealing rate: 1.5 K/s; total annealing time: $< 2 \text{ min}$.

As shown in Fig. 4, Δ^2 (and Δ) increases continuously with temperature in the regime between 100 and 300 K. In principle, such a temperature dependence is expected; see (1). A comparison of the experimental data with the dashed

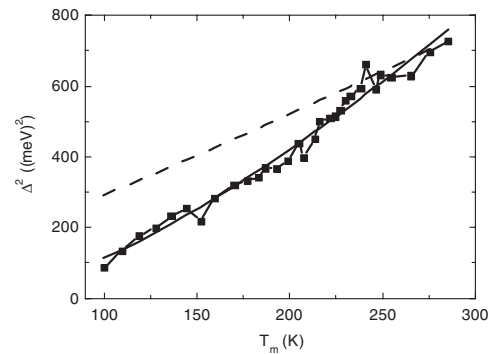


FIG. 4. The value of Δ^2 as a function of different measurement temperatures T_m for the HO-ZnO surface exposed to 1000 L atomic hydrogen at 100 K. The dashed line has been obtained using Eq. (1) assuming a temperature-independent density of carriers n_c . The solid line is the result of a nonlinear least squares fit assuming an ionization energy of the H-induced shallow donor of $\varepsilon_d = 25 \text{ meV}$ (see text).

line in Fig. 4, however, reveals that the temperature dependence predicted by (1) is much too small to reproduce the experimental behavior. The only possibility to explain this strong temperature variation is to assume that the carrier density itself n_c depends on temperature. This is in accord with previous suggestions, that H interstitials act as shallow donors with fairly small ionization energies [2].

For an n -type semiconductor, the CB charge density n_c can be calculated from [34,35]

$$n_c = \left(\frac{N_d N_c(T)}{2} \right)^{1/2} \exp(-\varepsilon_d/2k_B T) \quad (2)$$

$$\text{or } \ln n_c = \frac{1}{2} \ln \left(\frac{N_d N_{c,0}}{2} \right) - \frac{\varepsilon_d}{2k_B T} + \frac{3}{4} \ln T,$$

where N_d is the density of donor atoms, $N_c(T)$ the effective conduction band density of states, and $N_{c,0} = 2N_{c,0} T^{3/2}$, with $N_{c,0} = \left(\frac{m^* k_B}{2\pi \hbar^2} \right)^{3/2}$. ε_d denotes the donor state ionization energy. If we insert the expression for n_c in (2) into (1), we can perform a nonlinear least squares regression analysis, which yields $\varepsilon_d = 25 \pm 5$ meV. The latter value is in reasonable agreement with the ionization energy of 35 ± 5 meV as obtained from a completely different method, EPR [4]. This value, however, is substantially smaller than the value deduced from electrical conductivity experiments: 51 meV [11]. The higher value might result from contributions from other types of defects, such as oxygen vacancies, which are included in conductivity measurements.

In summary, our HREELS and TDS data demonstrate that exposing a fully hydroxylated ZnO(000 $\bar{1}$) surface to atomic hydrogen leads to the incorporation of subsurface interstitial H atoms. The shallow donor states created by this doping process can be thermally dissociated, thus populating the conduction band and, as a result, giving rise to plasmon losses seen in EELS. From the observed temperature dependence, an ionization energy of 25 ± 5 meV is obtained. In the future we will use this method to study the doping of ZnO by other elements, in particular, metals.

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