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Hydrogen motion in the Cu-H complex in ZnO

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The Cu-H complex in ZnO consists of Cu on Zn site and a hydrogen atom bound to a nearby O atom, with the O–H bond oriented in the basal plane of the hexagonal lattice to the c axis. The motion of hydrogen in the Cu-H complex is studied by the stress-induced dichroism. Stress applied at room temperature along $[1\bar{2}10]$ results in an alignment of the Cu-H bond. The reorientation process was found to be thermally activated with the activation energy of 0.52±0.04 eV. The connection of the hydrogen movement in the Cu-H complex with the hydrogen diffusion in ZnO is discussed, and consequences for the existence of interstitial hydrogen at room temperature are presented.

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I. INTRODUCTION

Hydrogen is a common impurity in ZnO that strongly influences its electrical and optical properties. For example, incorporation of hydrogen into ZnO results in enhancement of n-type conductivity: either via formation of shallow donor states or acceptor passivation.[1,2] At present, the nature of hydrogen-related shallow donors remains unclear,[3–5] whereas the microscopic structure of some acceptor-hydrogen complexes is well established.[6–12] In this paper, we study the properties of hydrogen in the Cu-H defect.[13]

In the ZnO lattice, Cu occupies a Zn site and gives rise to a deep acceptor level $(-/0)$ in the band gap at $E_c-0.17$ meV.[14–18] Since isolated hydrogen in ZnO is believed to be in the positive charge state and is mobile at room temperature, the two impurities easily form a family of Cu_n-H_m complexes.[6,7] Cu-H (with $n=1$, $m=1$) is the one that dominates the series.

The Cu-H defect is stable up to 650 °C.[8] Spectroscopically, it is characterized by an IR absorption line at 3192 cm^{-1} resulting from a local vibrational mode (LVM) of the O–H bond.[13] First-principles theory finds that Cu-H consists of a substitutional Cu atom at the Zn site with a bond-centered hydrogen sitting in the basal plane of the hexagonal lattice between substitutional Cu and O.[12]

Recently, uniaxial stress was employed to probe the microscopic structure of Cu-H.[19] The 3192 cm^{-1} mode was found to split in accordance with the proposed model of the defect. Based on the quantitative analysis of the stress effects, an energy level diagram of Cu-H was proposed. Interestingly, in addition to the main LVM at 3192 cm^{-1}, the defect has two low-energy excitations at 25 and 49 cm^{-1}, which manifest themselves with a stress parallel to the c axis.

At present, the kinetics of hydrogen in ZnO is a controversial issue. For example, an activation energy for hydrogen diffusion (E_a) ranges from 0.2 to 1.1 eV, determined by different techniques.[1,2,20,21] Such a discrepancy leads to contradictory conclusions about the stability of isolated hydrogen in ZnO: $E_a=0.2$ eV implies a very mobile species which is readily trapped in stable complexes already at liquid nitrogen temperatures, whereas $E_a=1.1$ eV means that isolated hydrogen could be found in ZnO at room temperature (RT).

First-principles calculations performed recently indicate that the activation energy for hydrogen diffusion in ZnO is below 0.5 eV, which suggests that isolated hydrogen cannot exist in ZnO at RT.[22] These results question the assignments of some IR absorption lines such as those originating from the isolated hydrogen species.[8,23]

We address the issue of the hydrogen mobility by studying, in this paper, the motion of hydrogen around substituted Cu in the Cu-H complex by means of the stress-induced dichroism technique. We show that a stress applied at elevated temperatures lifts the degeneracy of the complex between three equivalent crystallographic orientations of the O–H bond. Monitoring the reverse process at different temperatures reveals the activation barrier of the reorientation and provides insight into the hydrogen kinetics in ZnO. Similar experiments performed on acceptor-hydrogen complexes in Si (Refs. 24–27) and GaAs (Refs. 28 and 29) supplied important information on hydrogen in the semiconductor complexes.

II. EXPERIMENT

The samples employed in this study were hydrothermally grown n-type ZnO substrates obtained from CrysTec GmbH. They had sizes of $\sim 5.5\times 1.5\times 1.0$ mm^3, with the longer side parallel to $[1\bar{2}10]$. Cu doping was performed by annealing a sample at 1200 °C for 1 h in a sealed quartz ampoule filled with oxygen gas and a copper wire of ~ 1 mm^3 nearby. Subsequently, the samples were hydrogenated by annealing at 700 °C for 1 h in a sealed ampoule filled with hydrogen or deuterium. These anneals were terminated by quenching the ampoules to RT by water.

Uniaxial stress parallel to $[1\bar{2}10]$ was applied with a homebuilt stress rig placed in an exchange gas cryostat with ZnSe and KBr windows. The measurements were performed at ~ 10 K. Polarized light was produced by a wire-grid polarizer with a KRS-5 substrate in front of the cryostat.

Infrared absorption spectra were recorded with a BOMEM DA3.01 Fourier transform spectrometer equipped with a globar light source, a KBr beamsplitter, and a liquid-nitrogen-cooled InSb detector. The spectral resolution was 0.25 cm^{-1}.

For orientation (preferential alignment) of the Cu-H complex, uniaxial stress was applied at RT. Since at RT the defect

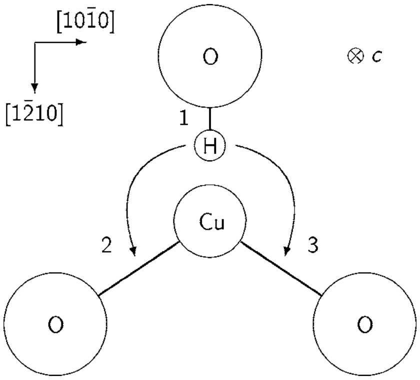

FIG. 1. Microscopic model of the Cu-H complex.

could be aligned within milliseconds, the stressing time was of no practical importance. While applying the stress, the sample was cooled down to ~10 K and the IR spectra were measured.

For reorientation (uniform distribution of O–H bonds comprising Cu-H), the sample was annealed for 30 min without stress at the temperature of interest ranging from 10 K to RT. Afterward, the sample was cooled down to 10 K again (the cooldown time was ~5 min), a stress of 0.3 GPa was applied, and the IR spectra were measured.

Two absorption spectra with electric field polarized either parallel or perpendicular to the stress were recorded after each annealing step and compared with reference spectra obtained for stress applied at ~10 K. Afterward, the sample was heated up without stress to RT to reinstall uniform distribution.

III. MODEL

The microscopic model of the Cu-H defect projected onto the c plane is shown in Fig. 1.[13] In the following consideration, we use the coordinate system with $\boldsymbol{x}\parallel[1\bar{2}10]$, $\boldsymbol{y}\parallel[10\bar{1}0]$, and $z\parallel c$.

Without perturbation, there are three equivalent orientations of the O–H bond ($n=1$, 2, or 3; see Fig. 1) in the Cu-H complex. Uniaxial stress applied along $[1\bar{2}10]$ ($\boldsymbol{F}\parallel\boldsymbol{x}$) lifts the degeneracy. In linear approximation, the energy of each orientation E_n depends on the stress as

$$E_n=\sum_{ij}B_{ij}^{n}\sigma_{ij}, \tag{1}$$

where $\boldsymbol{B}^n$ is the symmetric piezospectroscopic tensor of the Cu-H complex for the nth orientation. If we choose the first orientation as the basic one, then the components of $\boldsymbol{B}^{2(3)}$ could be obtained from $\boldsymbol{B}^1$ via rotation of the coordinate system by ±120° around the c axis. Since for $\boldsymbol{F}\parallel\boldsymbol{x}$ the only nonzero component of the $\boldsymbol{\sigma}$ tensor is $\sigma_{xx}=\sigma$, Eq. (1) is simplified to

$$E_n=B_{xx}^{n}\sigma. \tag{2}$$

The Cu-H complex is symmetric with respect to the reflection in the plane containing the c axis and the O–H bond. From this, it follows that $B_{xy}^1=B_{yz}^1=0$. We will omit the superscript at $\boldsymbol{B}^n$ in the further discussion since all the results are expressed via components of $\boldsymbol{B}^1$. Thus, we obtain

$$E_1=B_{xx}\sigma,$$

$$E_2=E_3=\frac{1}{4}(3B_{yy}+B_{xx})\sigma,$$

$$\Delta E=E_2-E_1=\frac{3}{4}(B_{yy}-B_{xx})\sigma. \tag{3}$$

The population ratio n_1/n_2 between the number of defects in configurations 1 and 2 is determined by the Boltzmann statistics,

$$n_1/n_2=\exp(\Delta E/kT). \tag{4}$$

Microscopically, the equilibrium distribution is achieved via jumps of hydrogen between the three possible positions around the Cu atom. The kinetics of this process is described by the following equations:

$$\frac{dn_1}{dt}=-2\frac{n_1}{\tau}+\frac{n_2}{\tau}+\frac{n_3}{\tau}=-2\frac{n_1}{\tau}+2\frac{n_2}{\tau},$$

$$\frac{dn_2}{dt}=\frac{n_1}{\tau}+\frac{n_3}{\tau}-2\frac{n_2}{\tau}=\frac{n_1}{\tau}-\frac{n_2}{\tau}. \tag{5}$$

Here, n_3 was replaced by n_2 because the two configurations are equivalent. The solution of these equations gives the ratio n_1/n_2 as a function of t, which in our experiment was 30 min. The time constant τ is assumed to depend on the temperature as

$$\tau^{-1}=\nu_0\exp(-E_a/kT). \tag{6}$$

Here, ν_0 is the "attempt frequency" and E_a is the activation energy for the jump. Normally, ν_0 is in the order of magnitude of the vibrational frequency of the defect,[30] which in the case of hydrogen is around 10^{13} s^{-1}.

Thus, monitoring the reorientation kinetics of the aligned Cu-H complex at different temperatures provides the attempt frequency ν_0 and the activation barrier E_a of hydrogen motion in the Cu-H complex.

IV. RESULTS

From Fig. 1, it is obvious that the uniaxial stress-induced response of the Cu-H complex depends on the O–H bond orientation. The effect of uniaxial stress on Cu-H at low temperatures was recently reported in Ref. 19. In particular, it was shown that the LVM of the defect splits into two components for $\boldsymbol{F}\parallel[1\bar{2}10]$.

Figure 2 represents the IR absorption spectra measured for the 3192 (2379) cm^{-1} LVM of the Cu-H (Cu-D) complex for $\boldsymbol{F}\parallel[1\bar{2}10]$. Component 1 corresponds to the case when the O–H bond of the defect is oriented "parallel" to the stress (see Fig. 1), whereas the one labeled 2,3 stands for those bonds aligned "perpendicular" to the stress.

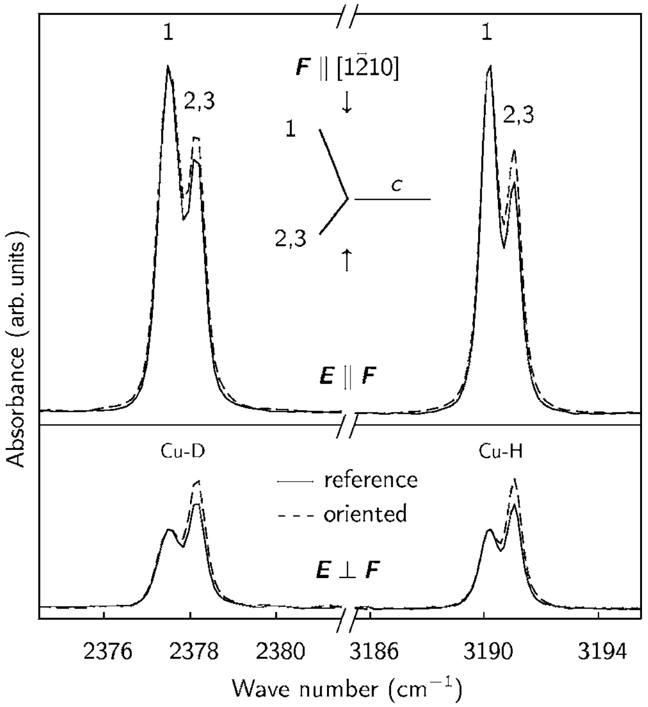

FIG. 2. IR absorption spectra of Cu-H (Cu-D) at 3192 cm^{-1} (2379 cm^{-1}) measured at T=10 K under 0.30 GPa uniaxial stress, $\boldsymbol{F}\parallel[1\bar{2}10]$ and $\boldsymbol{k}\parallel[10\bar{1}0]$. Solid line, stress applied at 10 K; dashed line, stress applied at RT before the sample was cooled down to the temperature of measurement. For convenience, each spectrum is normalized to the intensity of component 1.

The intensities of the two split-off components I_1 and $I_{2,3}$ depend on the angle ϑ formed by the c axis and the O–H bond of the Cu-H complex and the number of defects in each configuration n_1 and n_2 of the two different orientations. Note that we consider only these two configurations since, for $\boldsymbol{F}\parallel[1\bar{2}10]$, orientations 2 and 3 are equivalent. Normalized to the intensity of component 1, the intensities of the split-off lines are

$$
\begin{aligned}
I_1^{\parallel} &= n_1 \sin^2(\vartheta), \\
I_1^{\perp} &= n_1 \cos^2(\vartheta), \\
I_{2,3}^{\parallel} &= n_2 \sin^2(\vartheta)/2, \\
I_{2,3}^{\perp} &= 2n_2 \cos^2(\vartheta).
\end{aligned}
\tag{7}
$$

The superscripts "∥" and "⊥" label the intensities measured with the polarizer either parallel ($\boldsymbol{E}\parallel\boldsymbol{F}$) or perpendicular ($\boldsymbol{E}\perp\boldsymbol{F}$) to the stress. Previously, it was shown that $\vartheta = 110°$, which is very close to the perfect tetrahedral angle of 109.47°.[19]

The spectra shown in Fig. 2 by the solid line were measured when the stress was applied after the sample temperature reached 10 K. It follows from the figure that in this case, $I_1^{\parallel}/I_{2,3}^{\parallel}=1.70$ and $I_1^{\perp}/I_{2,3}^{\perp}=0.60$, whereas according to Eq. (7) the corresponding ratios should be 2 and 0.5. The deviations are, however, reasonably small and are explained by nonideal mounting of the sample in the optical path of the spectrometer.

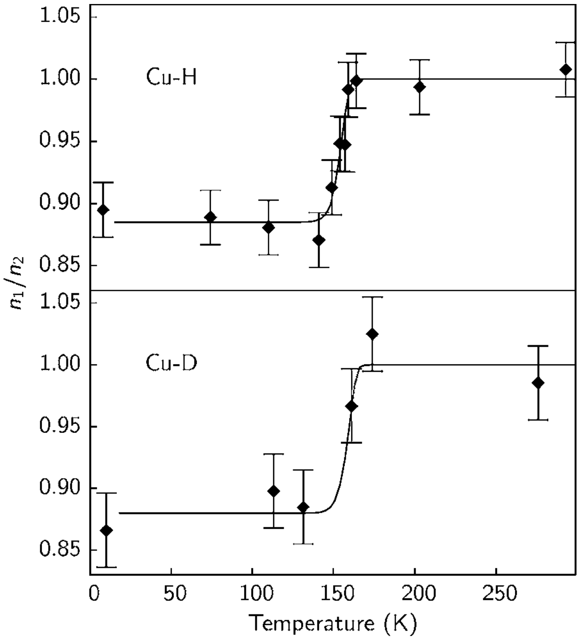

FIG. 3. Occupation ratio n_1/n_2 of the Cu-H (Cu-D) complex as a function of annealing temperature. The preliminary alignment was done at RT by a stress of 0.3 GPa. Annealing time is 30 min. The solid lines are fits obtained from Eqs. (5) and (6).

We show below that at 10 K no stress-induced orientation of Cu-H occurs. This means that n_1/n_2 is independent of stress and equals 1. However, if the stress is applied to the sample at RT before cooling down the sample to the temperature of measurements at 10 K, the situation changes.

The dashed line in Fig. 2 shows the effect of stress of 0.3 GPa applied to the same sample at RT. In this case, $I_1^{\parallel}/I_{2,3}^{\parallel}=1.51$ and $I_1^{\perp}/I_{2,3}^{\perp}=0.53$, which implies that $n_1/n_2 \approx 0.88$. According to Eq. (7), the reorientation should also result in a change of the integrated intensity of the 3192 cm^{-1} line: $I=I_1^{\parallel}+I_1^{\perp}+I_{2,3}^{\parallel}+I_{2,3}^{\perp}$. Indeed, within the error bars of our experiment, the observed intensity drop of the 3192 cm^{-1} signal by 2% is consistent with the value of $n_1/n_2 \approx 0.88$.

All these findings strongly indicate that the changes in the intensity ratios result from the stress-induced orientation. Since $n_1/n_2 < 1$, we conclude that the O–H bond of the Cu-H complex tends to flip to the orientation perpendicular to the stress.

Figure 3 shows the reorientation kinetics of the Cu-H (Cu-D) complex. Alignment was performed at RT by 0.3 GPa stress so that $n_1/n_2 \approx 0.88$. After that, the sample was annealed without stress for 30 min at a temperature in the range from 10 to 290 K. The alignment and annealing procedures have been repeated with different temperatures until $n_1/n_2=1$. It follows from the figure that, in the case of Cu-H, no reorientation occurs at temperatures below 150 K. For the Cu-D complex, the corresponding temperature seems

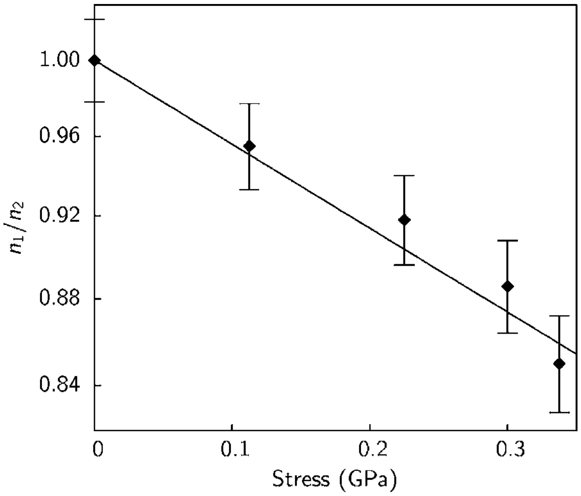

FIG. 4. Population ratio n_1/n_2 as a function of stress applied at room temperature.

to be 5 K higher, but the error bars do not allow us to conclude this with certainty. An enhancement of the reorientation temperature with replacement of hydrogen by deuterium is observed for acceptor-hydrogen complexes in Si and is normally attributed to zero-point energy effects.[26]

It follows from Fig. 3 that hydrogen motion in the Cu-H complex is thermally activated and tunneling is not a dominating mechanism resulting in the defect alignment under stress. Due to relatively large error bars, however, a combination of the two processes, so-called thermally activated tunneling, could not be ruled out.[31,32] Even so, from the studies of the acceptor-hydrogen complexes in Si, it is known that corrections to the Arrhenius-type behavior are small.[26] Equation (6) was employed to fit the experimental data presented in Fig. 3. The solid lines in the figure represent the best fit.

The attempt frequency has very little influence on the fitting curve. We assumed ν_0 in the range of 10^{11}–10^{13} s^{-1}. Such frequencies are typical for hydrogen-related defects in other semiconductors and characterize hydrogen vibrations.[24–29] The reorientation temperature, on the other hand, is very sensitive to the value of E_a. From the data shown in the figure, we find that $E_a = 0.52 \pm 0.04$ eV. The error bars come from the uncertainty in the attempt frequency: A change in ν_0 by a factor of 10 results in the shift of E_a by 0.03 eV.

Finally, we determined the population ratio n_1/n_2 as a function of stress applied at RT. Figure 4 shows the data. From Eqs. (3) and (4) and the data presented in the figure, we obtain $B_{xx} - B_{yy} = -8 \pm 2$ meV/GPa, which is close to the values found for acceptor-hydrogen complexes in Si and GaAs.[29,33,34] Note that in Eq. (4) we assumed $T = 155$ K since this is the temperature at which hydrogen motion around Cu freezes in.

V. DISCUSSION

It is interesting to compare our results with theory. To the best of our knowledge, the only theoretical study of hydrogen kinetics in ZnO was done by Wardle *et al.*, who investigated diffusion of isolated hydrogen.[22] Different migration paths in the ZnO lattice were considered, and it was found that the barrier of diffusion is less than 0.5 eV.

Of course, one cannot directly apply the results of Wardle *et al.* to the reorientation kinetics of hydrogen comprising the Cu-H complex. Even so, we believe that the two cases have some similarities.

Cu and Zn are next neighbors in the Periodic Table, with ionic radii differing only by 1%. Thus, we expect that the lattice distortion due to substitutional Cu is relatively small. Additionally, the Coulomb interaction within the Cu-H complex should not directly influence the hydrogen motion around Cu, since all three possible orientations of the O–H bond are equivalent.

If so, the barrier for hydrogen motion in the Cu-H complex ($E_a \approx 0.5$ eV) should be compared with the one corresponding to a jump between the neighboring bond-centered sites of the ZnO lattice perpendicular to the c axis. According to Wardle *et al.*, it is around 0.3 eV.

Wardle *et al.* found that hydrogen in ZnO is a very mobile species at temperatures well below 300 K. Thus, it prefers to form complexes with other impurities, which are abundant in state-of-the-art ZnO. This, in turn, implies that previous assignments of the isolated hydrogen species should be reconsidered.[8,23]

It is also interesting to compare our results on the Cu-H complex in ZnO with hydrogen kinetics in silicon. The activation energy of hydrogen diffusion in Si is around 0.48 eV,[35] which matches quite well the reorientation barrier of isolated bond-centered hydrogen, $E_a = 0.43 \pm 0.02$ eV.[36]

We want to compare this value with the reorientation barrier of H in the acceptor-hydrogen complexes in Si. Two defects, B-H and Al-H, were investigated and it was found that $E_a \approx 0.2$ eV for the B-H complex,[26] whereas $E_a = 0.37$ eV for hydrogen bound to Al.[27] Obviously, of these two complexes, it is Al-H that has to be compared with isolated hydrogen since Al and Si are next neighbors in the Periodic Table. Indeed, in this case, the activation barrier for hydrogen reorientation in the Al-H complex is only 20% off from E_a of isolated hydrogen.

Therefore, based on the analogy between Al in Si and Cu in ZnO, one might expect that the reorientation barrier for hydrogen in the Cu-H complex should not considerably deviate from the diffusion barrier of isolated hydrogen.

Contrary to the defects associated with the isolated hydrogen, the microscopic structure of Cu-H is well established from experiments. Therefore, the Cu-H complex seems to be an excellent candidate to experimentally verify theoretical predictions. Calculations on the hydrogen motion in the Cu-H complex are needed, which will help to relate our results on the reorientation barrier to the hydrogen diffusion in ZnO.

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