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Hydrogen donors in ZnO and TiO₂

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ABSTRACT

The results of combined IR absorption and photoconductivity studies on hydrogen donors in ZnO and TiO₂ are presented. It is shown that hydrogen donors in ZnO and rutile TiO₂ can be detected as Fano resonances in the photoconductivity spectra at the frequencies corresponding to the vibrational modes of these defects. In the case of anatase TiO₂ IR absorption lines at 3412 and 3417 cm⁻¹ are assigned to the stretching local vibrational modes of a donor in the neutral and the positive charge states, respectively. Interstitial hydrogen is suggested as a tentative model for the defect giving rise to these vibrational modes.

Keywords: ZnO, TiO₂, hydrogen

1. INTRODUCTION

Hydrogen is an inherent impurity in many metal oxides which strongly affects their electrical and optical properties. Typically, it binds to oxygen acting either as an amphoteric defect or as a donor.^{1–4} The latter is the case in ZnO where interstitial hydrogen (H_{BC}) and hydrogen substituting for oxygen (H_O) form shallow donor states in the band gap.^{1,5}

There are three main polymorphs of TiO₂ occurring in the nature: rutile, anatase, and brookite, with the former being the stable configuration, whereas the latter two—the metastable ones. Due to longer carrier lifetime, exciton diffusion length, higher electron mobility, higher catalytic activity anatase is the material of choice from the point of view of applications.^{6–9} Structure of hydrogen donors in rutile and anatase is significantly different, revealing differences between anatase and rutile in electrical, magnetic and optical properties.^{8,10,11} Theory finds that electrons in rutile can localize at a lattice Ti atom, forming a small polaron, which hops to neighboring lattice sites, whereas in anatase electrons prefer a delocalized state.^{12–14}

Local vibrational mode (LVM) spectroscopy is a versatile tool that provides a wealth of information about the chemistry and symmetry of light defects in the host lattice.¹⁵ Unfortunately, many LVMs are positioned in the strongly absorbing spectral regions, which does not allow to apply IR absorption spectroscopy to probe vibrational motion of impurities and defects. Recently, a method of photoconductive detection of LVMs has been proposed to overcome the challenges faced by IR absorption in ionic crystals.^{16,17} The method was applied to investigate LVMs of hydrogen substituting for oxygen in ZnO.

The principle of the method is shown in Fig. 1. A photocurrent is detected when an incoming photon excites an electron from the ground state of a donor into the conduction band of a semiconductor. Alternatively, a photon with the same energy can excite an LVM of the defect. If the two types of excitations are

Figure 1. Principles of detection of vibrational modes as Fano resonances in photoconductivity spectra of shallow donors.

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coupled the photoconductivity (PC) spectrum is modified resulting in a Fano resonance.¹⁸ The advantage of this method compared with the conventional IR absorption is the exceptional sensitivity of photoconductive techniques.¹⁹

The shape of the resonance is given by¹⁸

$$I(\epsilon) \propto \frac{(q + \epsilon)^2}{1 + \epsilon^2}, \quad \epsilon = \frac{\omega - \Omega - \Delta\Omega}{\Gamma/2}, \quad (1)$$

where Ω is the LVM frequency, Γ is the spectral width of the interacting discrete vibrational state, $\Delta\Omega$ is the additional shift, and q is the line shape parameter. For $q = 0$ the LVM will appear as an anti-resonance, whereas for $q \rightarrow \pm\infty$ it will have a Lorentzian shape.

Note, that the shape of the Fano resonance due to the local vibrational modes (parameter q in Eq. (1)) is independent of the coupling V between vibrational and electronic excitations and is determined solely by the properties of the host crystal.¹⁷

Here, the results of a combined IR absorption and photoconductivity studies of hydrogen donors in ZnO and TiO₂ are summarized.^{5,16,17,20}

2. EXPERIMENTAL DETAILS

The photoconductivity and IR absorption measurements were performed with a Bomem DA3.01 Fourier spectrometer equipped with a globar light source and a KBr or CaF₂ beamsplitter. The samples were positioned in an exchange-gas cryostat equipped with ZnSe windows. The frequency range 500–5000 cm⁻¹ could be covered.^{21,22}

The nominally undoped ZnO samples were grown from the vapor phase at the Institute for Applied Physics, University of Erlangen, Germany.²³ The rutile TiO₂ samples were commercial (110)-oriented wafers purchased from CrysTec GmbH (Germany) grown by the Verneuil technique with a resistivity above 10 MΩcm at room temperature. Anatase TiO₂ samples used in the present study were (100)-, (101)-, and (001)-oriented natural single crystals provided by SurfaceNet GmbH.

Hydrogen or/and deuterium was/were introduced into the samples via thermal treatments in sealed quartz ampules, filled with H₂, D₂, or H₂ + D₂ gas (pressure of 0.5 bar at room temperature). The treatments were performed at 450–800 °C within 1 to 6 hours and were terminated by quenching to room temperature in water. To produce ohmic contacts, the samples were first etched with orthophosphoric acid (ZnO) or KOH (TiO₂) for 1 min at room temperature. Afterwards, two contacts with an area of approximately 2 × 2 mm² were generated by scratching an In-Ga eutectic onto the sample surface.

Figure 2. Sections of photoconductivity spectra taken at $T \leq 10$ K on vapor phase grown ZnO samples treated at 750 °C for 1 h in H₂ (top), D₂ (mid), and H₂ + D₂ (bottom) gas.

3. ZINC OXIDE

3.1 Interstitial hydrogen

Interstitial hydrogen in ZnO is a shallow donor with an ionization energy of 53 meV.⁵ Spectroscopic features of interstitial hydrogen (H_{BC}) were documented in IR absorption, photoluminescence, and Raman scattering. Intrinsic $1s \rightarrow 2p_z$ (p_{xy}) donor transitions at around 330 cm⁻¹ were also detected in photoconductivity spectra

of hydrogenated ZnO samples. Concentration of H_{BC} can be obtained from the intensity of the 3611-cm^{-1} line in the IR absorption spectra.⁵ For the treatment performed at 750°C it equals approximately $3 \times 10^{17}\text{ cm}^{-3}$ what matches the solubility limit of hydrogen at this temperature.²⁴

Figure 2 presents sections of photoconductivity spectra taken on ZnO samples treated in H_2 (top), D_2 (mid), and $H_2 + D_2$ (bottom) gas at 750°C . These spectra reveal that LVM of interstitial hydrogen in ZnO can also be probed by means of photoconductivity. Importantly, photocurrent *enhances* at the frequencies of LVMs due to both H_{BC} and D_{BC} compared to the background current what unambiguously identifies these features as Fano resonances with the parameter $q \rightarrow +\infty$ (see Eq. (1)).

The assignment of the defect giving rise to the LVM at 3611 cm^{-1} to the hydrogen shallow donor was made on the basis of combined spectroscopic studies including IR absorption, Raman scattering, and photoluminescence measurements.⁵ The photocurrent spectra presented in Fig. 2 imply that a clue about the electrical activity of isolated hydrogen in ZnO could be obtained at much lower cost simply by recording photoconductivity spectra in the region typical for the LVMs of the defect.

3.2 Hydrogen substituting for oxygen

Figure 3 presents a spectrum of a vapor phase grown ZnO sample hydrogenated at 750°C for 1 hour in H_2 gas. The spectrum was background subtracted using a photoconductivity spectrum of a sample where no H_O was incorporated. Two dips at 742 and 792 cm^{-1} are seen, whose frequencies match the theoretical prediction for the LVMs of hydrogen substituting for oxygen in ZnO.^{25,26}

Frequencies of local vibrational modes are inversely proportional to the square root of the masses of vibrating species. This allows to verify the nature of the 742 and 792 cm^{-1} lines since electronic donor $1s \rightarrow 2p$ transitions of H_O practically do not change after replacement of hydrogen with deuterium. On the other hand, no absorption lines at 742 and 792 cm^{-1} are detected in the spectrum of the deuterium-treated ZnO which agrees with the assignment of these lines to the vibrational modes of hydrogen. Note that the expected local vibrational modes of D_O at about $742/\sqrt{2} = 525$ and $792/\sqrt{2} = 560\text{ cm}^{-1}$ are to be found within the Reststrahlen band of ZnO where practically no light can enter the sample,²⁷ which explains why these LVMs can be detected neither by photoconductivity nor IR absorption.

Further insight into the nature of the 742 and 792 cm^{-1} modes can be obtained from polarized photoconductivity measurements. The 742 cm^{-1} mode is polarized parallel, whereas the one at 792 cm^{-1} perpendicular to the c axis of the crystal. Based on this, the 742 cm^{-1} mode should be associated with the non-degenerate mode A_1 , whereas the one at 792 cm^{-1} transforms as the double degenerate mode E of the C_{3v} point group.

Figure 3. Sections of photoconductivity spectra taken at $T \leq 10\text{ K}$ on a vapor phase grown ZnO sample treated at 750°C for 1 h in H_2 gas.

4. TITANIUM DIOXIDE

4.1 Rutile TiO_2

Figure 4 shows sections of photoconductivity spectra taken on rutile TiO_2 samples treated in H_2 (top), D_2 (mid), and $H_2 + D_2$ (bottom) gas in the temperature range 450 to 520°C . The treatments give rise to the features with the frequencies corresponding to the LVMs of interstitial hydrogen and deuterium at around 3290 and 2445 cm^{-1} , respectively.

The photoconductivity spectra obtained for hydrogenated rutile samples imply that the behavior of interstitial hydrogen in this oxide is similar to that of in ZnO. In both materials LVMs of hydrogen appear as Fano resonances with $q \rightarrow +\infty$, which implies that hydrogen should be the main donor in the samples.

This sets an upper limit of 300 meV for the ionization energy of hydrogen in rutile (see Fig. 1). The lowest frequency at which the photocurrent is detected in our setup occurs at around 1000 cm^{-1} , which should further reduce the ionization energy of the interstitial hydrogen to 120 meV.

This conclusion is not in line with first principles calculations predicting a small polaron rather than shallow-donor-like behavior of an electron bound to the hydrogen donor in rutile.^{12,13} In order to explain the controversy between theory and electrical measurements revealing delocalized free electron behavior it proposed that there is an energy barrier confining an electron to its delocalized, metastable state and keeping it from accessing the small polaron regime at helium temperatures.^{28,29}

This model, however, does not explain the thin structure of the LVMs of hydrogen previously associated with a small polaron localized at three different nearby Ti sites around interstitial hydrogen.³⁰ Further theoretical and experimental investigations are necessary to solve the controversy about behavior of hydrogen in rutile TiO_2 .

4.2 Anatase TiO_2

Preliminary results on IR absorption of hydrogen-related defects in anatase TiO_2 were reported recently.³¹ A group of lines at 3358, 3359, 3373, and 3389 cm^{-1} was observed in as received material. Hydrogenation from H_2 gas at 450°C enhances these signals and gives rise to new lines at 3412 cm^{-1} and 3417 cm^{-1} . Isotope substitution experiments have shown that all these features represent stretch LVMs of the O-H bonds. The lines at 3412 cm^{-1} and 3417 cm^{-1} were assigned to the neutral and the positive charge states of a hydrogen donor labeled H-I. Fig. 5 shows the intensities of the two lines plotted as a function of temperature. The line at 3417 cm^{-1} gains intensity at the expense of the one at 3412 cm^{-1} as the temperature rises. This is a natural behavior for a donor becoming ionized with increasing temperature.

The solid line in the figure is a fitting curve calculated with an assumption that there is a zero charge density in the sample, whereby only electrons in the conduction band, ionized hydrogen donors, and compensating acceptors are charged. A possible contribution from other donors and that of the holes in the valence band was disregarded. Note that the compensation degree of $\gamma = 0.82$ was directly deduced from the relative intensities of the 3412-cm^{-1} and 3417-cm^{-1} lines at 6 K (see right panel in the figure). The best-fit curve was obtained with an ionization energy of around 17 meV. We emphasize, however, that this fit can serve only as a rough guide since besides the assumptions already made, the properties of electrons in the conduction band of anatase (e.g. density of states, polaronic effects, etc.) are either not well understood or remain unknown.

Figure 4. Sections of photoconductivity spectra taken at $T \approx 7\text{ K}$ on rutile TiO_2 samples treated in the temperature range 450 to 520°C for 1 h in H_2 (top), D_2 (mid), and $\text{H}_2 + \text{D}_2$ (bottom) gas.

Figure 5. (left) Integrated intensities of the 3412-cm^{-1} and 3417-cm^{-1} lines as a function of temperature. (right) Corresponding IR absorption spectra taken at 6 and 37 K. The spectra are offset vertically for clarity.

Theory finds that isolated hydrogen in anatase TiO₂ forms a hydroxyl ion with the direction of the O–H bond pointing nearly along the *a(b)*-axis.³² The hydrogen impurity level is located above the conduction band minimum, implying that it acts as a shallow donor.^{13,32} The vibrational mode of interstitial hydrogen was estimated to be at 3327 cm^{−1}, i.e. typical for most of the O–H units in metal oxides. Our experimental findings match the conclusions of theory thus making interstitial hydrogen a plausible model of the H-I defect.

Instability of hydrogen against annealing at 300 °C or storage at room temperature on the time scale of a few weeks is also in favor of interstitial hydrogen as a model of H-I. Theory suggests that the diffusion barrier of hydrogen in anatase TiO₂ is below or around 1 eV which makes it a highly diffusing species already at room temperature.³³ This implies that mobile H-I⁺ would readily form complexes with other impurities and defects, e.g. charged acceptors, explaining why the 3412- and 3417-cm^{−1} lines cannot be detected in as received material and in some as treated samples.

In summary, thermal stability, temperature dependences as well as isotope substitution experiments suggest that the likely origin of these lines are stretching local vibrational modes of the neutral and the positively charged interstitial hydrogen donor, respectively.

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