Electronic structure of the muonium center as a shallow donor in ZnO

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The electronic structure and the location of muonium centers (Mu) in single-crystalline ZnO were determined for the first time. Two species of Mu centers with extremely small hyperfine parameters have been observed below 40 K. Both Mu centers have an axial-symmetric hyperfine structure along with a ⟨0001⟩ axis, indicating that they are located at the AB_{O,∥} and BC_{⊥} sites. It is inferred from their small ionization energy (∼6 meV and 50 meV) and hyperfine parameters (∼10^{-4} times the vacuum value) that these centers behave as shallow donors, strongly suggesting that hydrogen is one of the primary origins of n type conductivity in as-grown ZnO.

Zinc oxide (ZnO) is one of the most promising semiconductors for the next generation of electronic and optoelectronic devices. It has already been applied to transducers, phosphors and varistors, due to its unique piezoelectric, optical, and electrical properties. In these applications, polycrystalline material has mainly been used. Moreover, recent progress in single crystal growth has opened up new possibilities, like bright blue and uv light emitters. Optical uv lasing has already been observed even at room temperature [2].

For applications to optoelectrical devices, it is crucial to control the bulk electronic conductivity of crystalline ZnO. However, it is notoriously difficult to obtain intrinsic ZnO, ending up with materials showing strong n type conductivity. In spite of more than 20 years of investigations, the origin of this unintentional carrier doping is still controversial. It has long been speculated that the dominant donor is a native defect, either oxygen vacancy, or zinc interstitial. Unfortunately, recent theoretical investigations have revealed that none of those native defects behave as shallow donors.

Recently, it was theoretically pointed out that hydrogen (H), which is quite difficult to remove from the crystal growth environment, is an excellent candidate for such a shallow donor [3,4]. As shown in Fig. 1, ZnO crystallizes in the wurtzite structure corresponding to an elongated zinc blend structure with hexagonal symmetry around the [0001] axis. The lattice parameters are known by experiments as a = 0.325 nm, c/a = 1.602 and u = 0.382 in normalized coordinates. From a first-principle calculation, the lowest energy configurations for hydrogen are predicted to be at the BC_{⊥} site, with a nearly equivalent formation energy for the BC_{∥}, AB_{O,⊥}, and AB_{O,∥} sites [6]. Experimental evidence for this scenario has been claimed in several reports [7–11], where an increase in the conductivity was observed upon introducing H into ZnO.

In this Letter we report on a determination of the electronic structure and the location of a muonium (Mu, an analogue of isolated hydrogen whose proton is substituted by a positive muon) as a shallow donor in ZnO. By using single-crystalline ZnO, two species of muonium have been clearly distinguished. The muonium center is readily observed in a wide variety of semiconductors after positive muon implantation, and has been serving as a unique source of information on the electronic structure of isolated hydrogen centers [12]. While the dynamical aspect (e.g., diffusion property) may be considerably different between Mu and H due to the light mass of Mu (∼1/2 m_{p}), the local electronic structure of Mu is virtually equivalent to that of H after a small correction due to the difference in the reduced mass (∼4%). It is now well established in elemental and III-V compound semiconductors that there are two stable (and metastable) sites, one at the center of the matrix bond (i.e., BC-site, Mu_{BC}^0) with a large outward relaxation of the nearest-neighbor (nn) host atoms, and the other around the center of a tetrahedron cage (i.e., T_{4} site, Mu_{T}^0). While Mu_{T}^0 has a large isotropic hyperfine parameter (almost the same order of the vacuum value, A_{μ} ≃ 4463 MHz), the hyperfine parameter of Mu_{BC}^0 has a value about one order of magnitude smaller with a large unpaired spin density distributed on the nn host atoms. Recently, a novel muonium state having an extremely small hyperfine parameter (10^{-4} × A_{μ}) has been reported in a II-VI compound semiconductor, CdS [13], suggesting that such a shallow Mu center (and H center as well) might be present in ZnO to serve as a donor.

The experiment was performed at the Meson Science Laboratory (located in KEK) which provides a pulsed (50 ns pulse width and 20 Hz repetition) beam of 100% spin-polarized muons with a beam energy of 4 MeV. The muon beam with longitudinal polarization was implanted into a single-crystalline wafer (40 mm diameter, 0.5mm thickness, [0001] orientation) of ZnO obtained from Eagle-Picher Industries, Inc. The conventional time differential muon spin rotation (μSR) measurements were performed under a magnetic field applied in two different orientations: one in the transverse direction (TF, B in Fig. 1) and the other in a tilted direction (B′) with respect to the initial muon spin polarization $\vec{P}_μ$. To obtain the tilted field, both transverse and longitudinal (LF) magnetic
fields were applied simultaneously. In the case of hyperfine parameter measurements, the specimen was placed on a cold finger with the [0001] axis parallel with \( \vec{P}_0 \) (O-face up). As shown in Fig. 1, the [1120] axis was set either perpendicular to \( \vec{B} \) (Fig. 1a) or parallel with \( \vec{B} \) (Fig. 1b) to examine the angular dependence of the hyperfine constants. For the temperature dependence measurements of the muonium fraction, the [0001] axis was tilted by 45° to \( \vec{P}_\mu \) (i.e., \( \vec{B}_{[0001]} = 45° \)) while \( \vec{B} \perp [1120] \).

It has been inferred from TF (=2.00 mT, 4.00 mT and 30.0 mT) measurements that only a single diamagnetic muon state is present above 40 K. The relaxation rate is almost independent of temperature with a rate of \( \sim 0.022(6) \mu \text{s}^{-1} \) for Gaussian damping, which is consistent with the dipole-dipole interaction of muons with \(^{67}\text{Zn}\) nuclei (natural abundance 4.1%). On the other hand, the muon spin rotation signal changes drastically with \( \vec{B}_{[0001]} \perp \vec{B} \) (where \( \theta = 54.0° \), \( \Delta \nu_1 = 495(2) \text{kHz} \), \( \Delta \nu_2 = 298(4) \text{kHz} \)), the rest of the hyperfine parameters are deduced to be

\[
A_1(90°) = |A_{1\parallel}| = 358(4) \text{kHz}, \quad (4) \\
A_2(90°) = |A_{2\perp}| = 150(4) \text{kHz}. \quad (5)
\]

Combining this result with the data under a tilted field \( \vec{B}' \) (where \( \theta = 54.0° \)), \( \Delta \nu_1 = 495(2) \text{kHz} \), \( \Delta \nu_2 = 298(4) \text{kHz} \), the rest of the hyperfine parameters are deduced as

\[
|A_{1\parallel}| = 756(13) \text{kHz}, \quad (6) \\
|A_{2\perp}| = 579(19) \text{kHz}. \quad (7)
\]

As shown in TABLE I, the angular dependence of the frequencies (\( \Delta \nu_i \)) calculated by the above parameters is in excellent agreement with the experimental observation.

The possibility that these Mu centers have a hyperfine tensor with the symmetry axis parallel to BC\(_\perp\) is eliminated by the fact that the observed precession frequency is independent of the rotation of the crystal around the [0001] axis by 90°. Another attempt to explain this by resorting to a sufficiently small anisotropy with the symmetry axis parallel to BC\(_I\) fails to account for the difference between \( A_{\parallel} \) and \( A_{\perp} \) consistently with the data. Thus, we conclude that there are two species of Mu centers, both of which have axially symmetric hyperfine structure along with the [0001] axis. Hereafter, we denote these two centers as Mu\(_I\) and Mu\(_II\) with the corresponding hyperfine parameters, \( A_I(\theta) \) and \( A_{II}(\theta) \), respectively. The static dielectric constants in ZnO are reported to be 7.8(3) for perpendicular and 8.75(40) for parallel to the [0001] axis \( \square \). The degree of obtained anisotropy for the muonium hyperfine tensor (\( \sim 50\% \)) is much larger than that of the dielectric constant (\( \sim 10\% \)), indicating that the anisotropy is determined by the local electronic structure with the BC\(_I\) and AB\(_I\parallel\) sites (see Fig. 1) being the most probable candidates for the sites of those Mu centers. Considering the magnitude of anisotropy in the hyperfine tensors, it would be reasonable to assume that Mu\(_I\) is located at the AB\(_O\perp\) site and Mu\(_II\) at the BC\(_I\) site. Let us compare our results to a simple model of shallow level centers in a dielectric medium. In this model, the hyperfine parameter is inversely proportional to the cube of the Bohr radius \( (a_d) \) of the bound electrons. The isotropic part of the hyperfine parameter, \( A_{so} (= |A_{1\parallel} + A_{2\perp}|/2) \), is 491 kHz for Mu\(_I\) and 293 kHz for Mu\(_II\). Compared with \( A_{p} = 4463 \text{ MHz} \), one obtains \( a_d = 21a_0 = 1.1 \text{ nm} \) for Mu\(_I\) and \( a_d = 25a_0 = 1.3 \text{ nm} \) for Mu\(_II\) (where \( a_0 \) is the Bohr radius of the free Mu). On the other hand, the Bohr radius for a hydrogen-like defect is calculated from the average dielectric constant,
\( \epsilon = 8.12 \), and the electron effective mass, \( m^* = 0.318 m_e \), of ZnO, i.e. \( a_d = (\epsilon/m_e/m^*)a_0 = 25.5 a_0 \). This value is qualitatively in good accord with those of Mu\(_I\) and Mu\(_{II}\).

The temperature dependence of the amplitudes of Mu\(_I\), Mu\(_{II}\), and diamagnetic muon are plotted in Fig. 4. The total yield of all states are almost independent of temperature, suggesting that Mu\(_I\) and Mu\(_{II}\) are ionized to a diamagnetic muon above the transition temperature(\( \sim 40 \) K). It is unlikely that these Mu energy levels are just above the valence band. Otherwise, the temperature dependence of the muonium charge state would not be expected due to the \( n \) type conductivity of the present specimen where the Fermi level is much higher than the mid-gap level. These results indicate that the Mu centers act as shallow level donors. Thus, since Mu centers simulate the electronic structure of H in ZnO, our result provides convincing evidence that the hydrogen centers in ZnO are shallow donors, leading to \( n \) type conductivity in ZnO.

The activation energies of Mu\(_I\) and Mu\(_{II}\) were obtained to be 3 meV and 25 meV, respectively from the data in Fig. 4. According to the analysis in [13], the relation \( E_d = 2E_a \) is satisfied between the defect level energy \( (E_d) \) and the activation energy \( (E_a) \), which leads to the respective defect level energies of Mu\(_I\) and Mu\(_{II}\) to be 6 meV and 50 meV. The latter is fairly consistent with the calculated value of the hydrogen-like impurity model, 13.6\((m^*/m_e/\epsilon^2) = 66 \) meV, and the observed value of 61 meV attributed to H in an earlier report [1]. Considering the large ambiguity in determining the defect level energy for another donor at 31 meV which has a much lower concentration in ZnO, Mu\(_I\) may correspond to this shallower donor.

The reason for the absence of Mu centers at other interstitial sites is yet to be understood. Another issue is that a large fraction of diamagnetic muons (about 50\%) exists even at the lowest temperature. One of the possibilities is that muon-oxygen bounding is formed, which has been commonly observed in various oxides. The other is that the diamagnetic centers may correspond to those at the BC\(_\perp\) or AB\(_\perp\) sites, where their defect energy levels are in the conduction band and/or their hyperfine parameters are too small to observe in our experiment. Further experiments, including \( \mu \)SR measurements at different geometry, would be helpful to address these issues. Meanwhile, more accurate theoretical investigations are strongly required to unambiguously identify the observed Mu centers.

In summary, we have demonstrated that two species of muonium centers are formed in ZnO below 40 K with extremely small hyperfine parameters. These centers have an axially symmetric hyperfine interaction around the [0001] axis. The temperature dependence of their fractional yields indicates that they act as shallow donors, strongly suggesting that hydrogen is the primary origin of unintentional \( n \) type conductivity in ZnO.

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Note added: After submission of this manuscript, the presence of a muonium state in the powder sample of ZnO was reported by a separate group [16].

\[ \epsilon = 8.12, m^* = 0.318 m_e, \]

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[1] D. C. Look, D. C. Reynolds, J. R. Sizelove, C. W. Litton, G. Cantwell and W. C. Harsch, Solid State commun. 105, 399 (1998).

[2] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen and T. Goto, Appl. Phys. Lett. 70, 2230 (1997).

[3] For a review, G. Heiland, E. Mollwo and F. Stöckmann, in Solid State Physics (Academic, New York, 1959), vol. 8, p.191.

[4] D. C. Look, J. W. Hemskey and J. R. Sizelove, Phys. Rev. Lett. 82, 2552 (1999).

[5] A. F. Kohan, G. Ceder, D. Morgan and C. G. Van de Walle, Phys. Rev. B 61, 15019(2000).

[6] C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000).

[7] E. Mollwo, Z.Phys. 138, 478 (1954).

[8] D. G. Thomas and J. J. Landor, J. Chem. Phys. 25, 1136 (1956).

[9] J. I. Landor, Chem. Solids 3, 87 (1957).

[10] S. J. Baik, J. H. Jang, C. H. Lee, W. Y. Cho and K. S. Lim, Appl. Phys. Lett. 70, 3516 (1997).

[11] S. Kohiki, M. Nishitani, T. Wada and T. Hirao, Appl. Phys. Lett. 64, 2876(1994).

[12] For reviews, B.D.Patterson, Rev. Mod. Phys. 60,69(1988); R.F.Kiefl and T.L.Estle, in Hydrogen in Semiconductors (Academic, San Diego, 1991).

[13] J. M. Gil, H. V. Alberto, R.C. Vilão, J. Pirote Duarte, P. J. Mendes, L. P.Foreira, N. Ayres de Campos, A. Weidinger, J. Krause, Ch. Niedermayer and S.F.J. Cox, Phys. Rev. Lett. 83, 5294 (1999).

[14] D. Eason (Eagle-Pichier Technologies) ; private communications.

[15] D. L. Rode, Semiconductors and Semimetals, 10, 1(1975).

[16] S.F.J.Cox, E.A Davis, S.P.Cottrell, P.J.C.King, J.S.Lord, J.M.Gil, H.V.alberto, R.C.Vilão, J. Pirote Duarte, N. Ayres de Campos, A. Weidinger, R.L. Lichti and S.J.C. Irvine, Phys. Rev. Lett. 86, 2601 (2001).
FIG. 1. The crystal structure of ZnO and the geometry of \(\mu\)SR measurements. The [0001] axis is parallel with the initial muon polarization \(\vec{P}_\mu\), while the transverse field \(\vec{B}\) is either (a) perpendicular to or (b) parallel with [11\(\bar{2}\)0] axis. Tilted field \(\vec{B}'\) is in a plane defined by \(\vec{B}\) and \(\vec{P}_\mu\). “BC” refers to the bond center sites and “AB” to the anti-bonding sites.

FIG. 2. \(\mu\)SR time spectrum in ZnO at 5.0 K, where the external field \(\vec{B}\) (|\(\vec{B}\)| = 30.0 mT) was applied 45° to the [0001] axis. A fitting result with two species of muonium centers are shown with corresponding errors (difference between data and fitted curve).

FIG. 3. FFT amplitude of the time spectrum at (a) 5.0 K, (b) 20 K, and (c) 46 K, obtained with TF=30.0mT, where arrows indicate the satellite peaks.

FIG. 4. The fractional yield of \(\text{Mu}_I\) (open triangle), \(\text{Mu}_{II}\) (open square) and a diamagnetic muon (closed circle) versus temperature in ZnO.

| Table I. Hyperfine splitting of muonium centers in ZnO, where the measured values are compared with those calculated from a particular set of hyperfine parameters. |

| configuration  | \(\theta\) | \(\Delta \nu_{1\text{cal}}\) | \(\Delta \nu_{1\text{exp}}\) | \(\Delta \nu_{2\text{cal}}\) | \(\Delta \nu_{2\text{exp}}\) |
|---------------|----------|----------------|----------------|----------------|----------------|
| \(B \perp \[11\bar{2}0\]\ (Fig.1a) | 90.0° | 358(4) | 358(4) | 150(4) | 150(4) kHz |
| \(B \perp \[11\bar{2}0\]\ (Fig.1a) | 54.0° | 495(7) | 495(2) | 298(8) | 298(4) kHz |
| \(B \parallel \[11\bar{2}0\]\ (Fig.1b) | 90.0° | 358(4) | 356(2) | 150(4) | 153(4) kHz |
| \(B \perp \[11\bar{2}0\]\ = 42.4° (1b) | | 539(8) | 541(4) | 345(9) | 350(4) kHz |