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 $\langle 0001 \rangle$ axis, indicating that they are located at the antibonding ($AB_{O,\parallel}$) and bond-center ($BC_{\parallel}$) sites. It is inferred from their small ionization energy ($\simeq 6$ and 50 meV) and hyperfine parameters ($\sim 10^{-4}$ 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.

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Zinc oxide (ZnO) is one of the most promising semiconductors for the next generation of electronic and optelectronic 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 [1] 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 [3,4]. Unfortunately, recent theoretical investigations have revealed that none of those native defects behaves as shallow donor [5].

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 [6]. 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 $BC_{\perp}$ site, with a nearly equivalent formation energy for the $BC_{\parallel}$, $AB_{O,\perp}$, and $AB_{O,\parallel}$ 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 analog 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 ($\simeq \frac{1}{9} m_p$), 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 ($\sim 4\%$). 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^0_{BC}) with a large outward relaxation of the

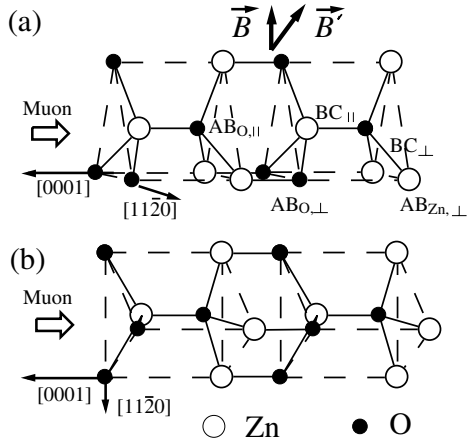

FIG. 1. The crystal structure of ZnO and the geometry of μSR measurements. The [0001] axis is parallel with the initial muon polarization $\vec{P}_{\mu}$, while the transverse field $\vec{B}$ is either (a) perpendicular to or (b) parallel with [11$\bar{2}$0] axis. Tilted field $\vec{B}'$ is in a plane defined by $\vec{B}$ and $\vec{P}_{\mu}$. "BC" refers to the bond-center sites and "AB" to the antibonding sites.

nearest-neighbor (nn) host atoms, and the other around the center of a tetrahedron cage (i.e., T_d site, Mu_T^0). Recently, a novel muonium state having an extremely small hyperfine parameter ($10^{-4} \times A_\mu$) 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, 0.5 mm 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, $\vec{B}$ in Fig. 1) and the other in a tilted direction ($\vec{B}'$) with respect to the initial muon spin polarization $\vec{P}_\mu$. 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 $\vec{P}_\mu$ (O-face up). As shown in Fig. 1, the $[11\bar{2}0]$ axis was set either perpendicular to $\vec{B}$ [Fig. 1(a)] or parallel with $\vec{B}$ [Fig. 1(b)] 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., $\vec{B} \angle [0001] = 45°$) while $\vec{B} \perp [11\bar{2}0]$.

It has been inferred from TF (= 2, 4, and 27 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 $\simeq 0.022(6)\ \mu s^{-1}$ for Gaussian damping, which is consistent with the dipole-dipole interaction of muons with ^{67}Zn nuclei (natural abundance 4.1%). On the other hand, the muon spin rotation signal changes drastically below 40 K. A typical μSR spectrum is shown in Fig. 2 with fit errors, where the data were obtained under 27 mT with $\vec{B} \angle [0001] = 45°$. Figure 3 shows the angular and temperature dependence of the frequency transform obtained by maximum entropy method (MEM) [14], in which two pairs of satellite lines are seen with their position situated symmetrically around the central line corresponding to the precession of diamagnetic muons (with the gyromagnetic ratio $\gamma_\mu = 2\pi \times 135.53$ MHz/T). The splitting of these satellites remained unchanged when the applied field was changed to 2 or 4 mT. Moreover, a nearly equivalent frequency spectrum was observed when the specimen was rotated by 90° around the [0001] axis [i.e., between Figs. 1(a) and 1(b)]. These results strongly suggest that two muonium centers with extremely small anisotropic hyperfine parameters exist in ZnO. The hyperfine parameters are about 10^{-4} times smaller than the vacuum value, and they are symmetric to the [0001] axis.

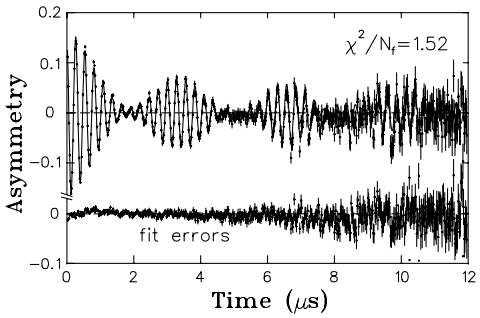

FIG. 2. μSR time spectrum in ZnO at 5.0 K, where the external field $\vec{B}$ ($|\vec{B}| = 27$ mT) was applied 45° to the [0001] axis. A fitting result with two species of muonium centers are shown with corresponding errors (difference between data and fitted curve).

Provided that the hyperfine interaction has an axial symmetry, we expect two muonium precession signals for the high-field limits with frequencies

$$\nu_-(\theta) \simeq \nu_0 - \tfrac{1}{2}\Delta\nu(\theta), \tag{1}$$

$$\nu_+(\theta) \simeq \nu_0 + \tfrac{1}{2}\Delta\nu(\theta), \tag{2}$$

$$\Delta\nu(\theta) = A(\theta) = |A_\parallel \cos^2\theta + A_\perp \sin^2\theta|, \tag{3}$$

where $2\pi\nu_0 = \gamma_\mu B$ with $B = |\vec{B}|$ being the applied field

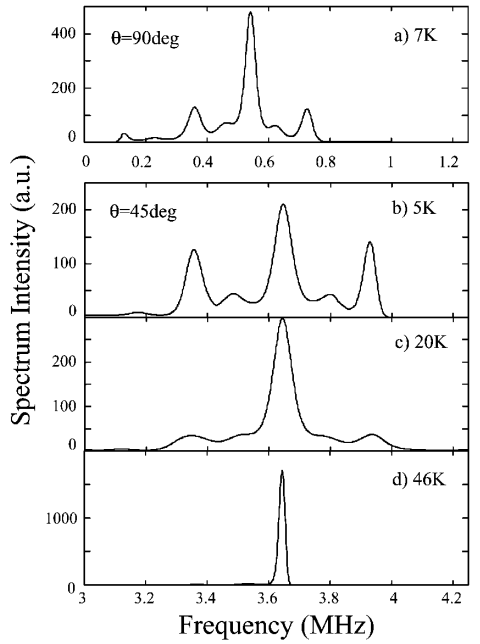

FIG. 3. Frequency spectrum obtained by the maximum entropy method for ZnO at (a) 7.0 K with $TF = 4$ mT perpendicular to [0001] axis, and those at different temperatures (b)–(d) with $TF = 27$ mT 45° tilted to the [0001] axis.

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	θ	$\Delta\nu_{1\mathrm{cal}}$	$\Delta\nu_{1\mathrm{exp}}$	$\Delta\nu_{2\mathrm{cal}}$	$\Delta\nu_{2\mathrm{exp}}$
$B \perp [11\bar{2}0]$ [Fig. 1(a)]	90.0°	358(4)	358(4)	150(4)	150(4) kHz
$B \perp [11\bar{2}0]$ [Fig. 1(a)]	54.0°	495(7)	495(2)	298(8)	298(4) kHz
$B \parallel [11\bar{2}0]$ [Fig. 1(b)]	90.0°	358(4)	356(2)	150(4)	153(4) kHz
$B\angle[11\bar{2}0] = 42.4°$ [Fig. 1(b)]	47.6°	539(8)	541(4)	345(9)	350(4) kHz

($B \gg 2\pi A/\gamma_e$, where $\gamma_e = 2\pi \times 28.024$ GHz/T is the gyromagnetic ratio of electron), θ is the angle between $\vec{B}$ and the symmetry axis [0001], and $A_\parallel$ and $A_\perp$ are the hyperfine parameters parallel and normal to [0001], respectively. It was revealed upon preliminary analysis that the fitting of μSR time spectra assuming the three frequency components (ν_0, ν_-, and ν_+) did not reproduce the time spectrum, yielding a large fraction ($\sim 20\%$) of fit errors and poor reduced χ^2 ($\simeq 2.40$). On the other hand, as suggested in Fig. 3(a), fitting analysis with two sets of satellites including five components (ν_0, ν_{i-}, and ν_{i+}, $i = 1, 2$) turned out to yield a satisfactory result with drastically improved χ^2 ($\simeq 1.52$). This indicates that there are two species of Mu centers with respective fractional yields in this compound. From the spectrum with $\vec{B} \perp [11\bar{2}0]$ [Fig. 1(a)], the hyperfine parameters are deduced to be

$$A_1(90°) = |A_{1\perp}| = 358(4) \text{ kHz}, \tag{4}$$

$$A_2(90°) = |A_{2\perp}| = 150(4) \text{ kHz}. \tag{5}$$

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

$$|A_{1\parallel}| = 756(13) \text{ kHz}, \tag{6}$$

$$|A_{2\parallel}| = 579(19) \text{ kHz}. \tag{7}$$

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 $BC_\perp$ 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, $A_1(\theta)$ and $A_2(\theta)$, 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 [15]. 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 $BC_\parallel$ and $AB_{O,\parallel}$ 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 presume that Mu_I is located at the $AB_{O,\parallel}$ site and Mu_{II} at the $BC_\parallel$ 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_{iso} ($= \frac{1}{3}A_\parallel + \frac{2}{3}A_\perp$), is 491 kHz for Mu_I and 293 kHz for Mu_{II}. Compared with $A_\mu = 4463$ MHz, one obtains $a_d = 21a_0 = 1.1$ nm for Mu_I and $a_d = 25a_0 = 1.3$ nm for Mu_{II} (where a_0 is the Bohr radius of the free Mu). On the other hand, the Bohr radius for a hydrogenlike defect is calculated from the average dielectric constant, $\epsilon = 8.12$, and the electron effective mass, $m^\star = 0.318m_e$, of ZnO [16], i.e. $a_d = (\epsilon/m_e/m^\star)a_0 = 25.5a_0$. 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

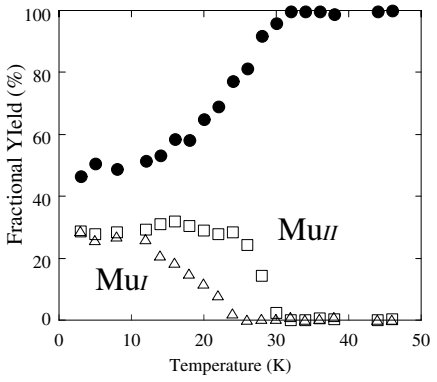

FIG. 4. The fractional yield of Mu_I (open triangles), Mu_{II} (open squares), and a diamagnetic muon (closed circles) versus temperature in ZnO.

diamagnetic muon above the transition temperature (~ 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 midgap 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 and 25 meV, respectively, from the data in Fig. 4. According to the analysis in Ref. [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 and 50 meV. The latter is fairly consistent with the calculated value of the hydrogenlike impurity model, $(13.6\ \text{eV}) \times (m^*/m_e/\epsilon^2) = 66$ 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 Ref. [1], 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 bonding is formed, which has been commonly observed in various oxides [17,18]. 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 μSR 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 [19].

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