Electronic structure of superconducting InN

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Abstract

We report on an investigation of superconductivity in n-type InN. There is an optimum carrier density for the occurrence of the superconductivity. The lowest carrier density is limited by the Mott transition of \( n_c \approx 2 \times 10^{17} \) \( \text{cm}^{-3} \) and the highest density is limited by the superconductor to insulator transition of \( n_c \approx 5 \times 10^{20} \) \( \text{cm}^{-3} \). We propose a mechanism where the occurrence of the superconductivity is related to the presence of In–In chains of finite length in the \( ab \) plane. The In–In chains, which originate from the inversion domains of InN grown on sapphire (0 0 0 1) and elongate along \( [\bar{1} 1 2 0] \), are coupled to form micro Josephson-junctions.

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1. Introduction

Among the group III-nitride semiconductors, InN is a key material for optical and high temperature device applications [1]. In most of the reports InN has been grown on sapphire (0 0 0 1) substrates and it is an n-type semiconductor in degenerate condition. Its crystal structure is hexagonal with the \( c \)-axis parallel to the substrate \( c \)-axis. The band gap energy was reported in earlier studies to be 1.9 eV [2,3]. With the recent development of a molecular beam epitaxy (MBE) growth method of InN, the crystal quality has greatly improved and has enabled us to reveal that the band gap energy of InN is less than 1.0 eV [4] and now it is believed to be 0.64 eV [5,6]. Recently, it was found that InN shows a Mott transition at \( n_c = 2 \times 10^{17} \) \( \text{cm}^{-3} \) from the carrier density (\( n_c \)) dependence of zero temperature conductivity [7]. For the determination of \( n_c \), however, a constant carrier density spread in the \( ab \) plane had to be excluded. The constant carrier density, though it seems to be originated from extrinsic property of semiconducting InN, generates strong Shubnikov–de Haas (SdH) oscillation which is observed only when the magnetic field is applied perpendicular to the \( ab \) plane.

Since it was reported that InN with a narrow band gap energy showed type II superconductivity below 3 K [4], it has been generally accepted that the superconductivity might be the result of the segregation or micro-network of metal In in InN. The magnetic field where the resistivity tends to zero, however, is much larger than that of metal In of 0.03 T [8]. This suggests that the superconductivity does not originate simply from metal In but that some anisotropic electronic structure with a strong electron–phonon interaction should exist.

The phonon structure of InN is clear and we have reported all the six optical phonons of hexagonal InN [9,10]. The acoustic-phonon branches are well separated from the optical ones due to the different mass mismatches between indium and nitrogen. The phonon structure is well reproduced by ab initio calculation and the agreement with the experimental results is very good [11]. The electron–phonon interaction of InN, however, is not so simple; when the optical phonon vibrates in the \( ab \) plane (\( E_1 \) mode), it couples with free carriers linearly, while when it vibrates along \( c \)-axis (\( A_1 \) mode), it couples nonlinearly with free carriers. The interaction mechanism is still under investigation [6,12].

In this report, we will present \( n_c \) dependence of the superconducting transition temperature based on the
previous reports. To make clear the superconducting properties of InN, we compare the magnetoresistance of InN which shows superconductivity with that which does not. We will discuss the possibility of a structure-sensitive low-dimensional metallic band in InN based on the results of SdH oscillation, and propose a mechanism of the anisotropic superconductivity in terms of the metallic band which, originating from the inversion domain of InN, forms in the ab plane of In atoms.

2. Experimental procedure

The InN investigated was grown on sapphire (0001) substrates by MBE and MOCVD methods [13–18]. The film resistance was measured by a standard four-terminal technique using a DC and lock-in amplifier at low frequency. The temperature dependence of the resistance was measured at the Grenoble High Magnetic Field Laboratory using a dilution refrigerator with in situ rotation in a 23 T resistive magnet and at the High-Field Laboratory for Superconducting Materials of Tohoku University using a He3 cryostat equipped with a 15 T superconducting magnet. All of the InN films had a hexagonal structure and their c-axis was perpendicular to the sapphire (0001) plane. The orientation of InN was parallel to that of Al2O3. The lattice constants of InN were determined from four reflections with a large diffraction angle and we obtained 3.53(6) Å for a-axis and 5.70(9) Å for c-axis as an average of the investigated samples. These values are much smaller than those reported by Tansley et al. (a = 3.548 Å, c = 5.760 Å) [3], whose samples were prepared by sputtering methods.

3. Results

3.1. Electron density dependence of the superconducting transition temperature

When InN shows superconducting transition, the temperature dependence of the resistivity is not very sharp so that we determine the superconducting transition temperature (Tc) where the resistivity becomes half of that of normal state. When the resistivity does not reach 50% at the lowest temperature of the measurements, we estimate Tc from the extrapolation. When the resistivity change is less than 10% at 0.5 K, we set Tc = 0 K. We plot thus defined Tc as a function of ne using the reported data in Fig. 1. All of the samples show a transition temperature below 3.4 K, Tc of bulk In. There is an optimum carrier density for the occurrence of superconductivity. At present there is no report of InN with a carrier density lower than ne = 4 \times 10^{17} \text{cm}^{-3}, and the sample with this ne becomes superconductor at Tc = 0.5 K. Hence the lowest limit of the transition should be ne.

As for the highest limit of ne, we have reported the existence of the superconductor to insulator transition around 5 \times 10^{20} \text{cm}^{-3} [21], which is shown in Fig. 2, where the temperature dependence of the resistivity of the samples having similar carrier densities are compared. These samples were grown by MOCVD under almost the same growth condition and hence the difference of ne is not essential for the occurrence of the superconductivity [13]. For Ref. [13], more than 40 samples were measured (not listed in the table) and most of them did not show superconductivity. Their ne was about 5–9 \times 10^{20} \text{cm}^{-3}, and so we can say that when ne is larger than 5 \times 10^{20} \text{cm}^{-3}, most InN samples remain in metallic condition, where their resistivity does not show temperature dependence. Sample no. 692 starts to show a small resistivity decrease at 3.4 K, and shows a superconducting transition at 1.5 K and reaches zero resistivity at 0.5 K. When the sample contains polycrystalline phases (no. 757), it shows a very steep and clear resistive change at 3.4 K. On
the other hand, no. 753 which has a less polycrystalline phase, shows a gradual decrease of resistivity around 3 K and reaches zero resistivity at 1.8 K. The resistivity of no. 680 increases below 3.4 K and this sample changes into insulator at 0.5 K. The ratio of the resistivity change below 3.4 K is more than one order of magnitude higher than that observed in non-doped InN, where the resistivity increase is caused by carrier localization [7]. Hence we conclude that the resistivity increase of no. 680 should be due to the localization of carriers in a form of Cooper pairs, because other samples with similar $n_e$ show decrease of resistivity due to the Bose condensation of Cooper pairs below 3.4 K. At present the major parameter for the occurrence of the superconducting transition is not clear yet, but apparently there is a disorder induced superconductor-insulator transition around $n_e/C_2^{10^{20}} cm^{-3}$.

3.2. Electron localization in non-superconducting InN

As is shown in Fig. 1, some samples do not show superconductivity [7]. These samples have an additional electronic structure together with a spherical Fermi surface. The additional electronic structure has anisotropic electronic distribution in the $ab$ plane with the anisotropy originating from the electron localization. Typical electron localization is shown in Fig. 3, where the InN ($#252$) shows metallic conduction above 40 K. Below 40 K, the resistivity ($\rho$) changes to insulator behavior and continues to change smoothly down to 0.5 K without showing any saturation (Fig. 3(a)). The temperature dependence of $\rho$ is given by $\rho \sim \log(1/T)$ which is expected from the two-dimensional localization and not by $\rho \sim \exp(T_0/T)^{1/4}$ which is expected from the variable range hopping conduction mechanism.

To make clear the electron localization effect in InN, we measured the temperature dependence of the transverse magnetoresistance (TMR), which is shown in Fig. 3(b). The applied magnetic field ($B$) was perpendicular to the $ab$ plane and the probing current was $[10\bar{1}0]$. When the temperature is higher than 4 K, the TMR shows a positive and monotonous behavior in the small $B$ region, where the monotonous part normalized to $\rho_0$ is proportional to $B^2$.

The TMR changes into a linear dependence in the high-field region, where a sinusoidal variation of resistance due to SdH oscillations is observed. When the temperature is lower than 3 K, a negative magnetoresistance (NMR) becomes observable in the small $B$ region. Angle dependence between the field and the $c$-axis of the NMR was reported previously and the observed NMR was concluded to be due to the localization of electrons in the $ab$ plane [7]. The frequency and the amplitude of SdH are not dependent on temperature. The Hall carrier density $n_H$, however, shows a strong temperature dependence between 4.2 and 3 K and $n_H$ at 3 K becomes almost one tenth of that obtained at 4.2 K. Hence there is a big and drastic change in the electron distribution between 4.2 and 3 K in the InN which does not show superconducting transition.

4. Discussion

From the angle dependence of the SdH signal, we have proposed a band structure at the fundamental gap [7], which is shown in Fig. 4. For the drawing, we use the band gap energy of 0.64 eV assuming a non-parabolic dispersion for the conduction band so as to meet the $n_e$ dependence of the photoluminescence spectra, where the energy parameter related to the momentum matrix element ($E_p$) is 10 eV [22]. The SdH oscillation shows that InN has a spherical Fermi surface with radius $k_A$ that increases according to the increase of $n_e$, which is denoted by $A$. The structure observed when the field is perpendicular to the $a-b$ plane is drawn as a flat ellipsoid with the largest radius $k_B$, which is denoted by $B$. The effective mass of $B$ is

![Fig. 3.](image-url)
The superconductivity of BCS theory is based on the Thomas–Fermi screening of electrons, where the screening energy is given by $1/k_F$ increases according to the increase of $n_e$, while $k_B$ does not. This suggests $B$ has a limited volume and is fully occupied, and that the carriers introduced into the sample lift the Fermi level of $A$. The structure is connected to the Fermi surface and the electrons belonging to $B$ can migrate into the $a-b$ plane. In order words, the band $B$, which will be explained later, is caused by In–In chains. The bands and charge-density-wave instability at low temperatures, bands $A$ and $B$ are connected electrically, because In–In chains are embedded in InN. When the temperature decreases, the difference between these two bands becomes obvious and the electrons belonging to $B$ localize as is shown in Fig. 3. Below 3.4 K they contribute to the negative magnetoresistance, Cooper pair generation and the superconductivity. These two energy bands with different characteristics are shown in Fig. 4 in an exaggerated manner in energy.

The superconductivity of BCS theory is based on the Thomas–Fermi screening of electrons, where the screening length is given by $1/k_F$. As is reported before [7], $1/k_F$ of InN is $\sim 100 \, \text{Å}$, which is much larger than the value of conventional ($\sim 1 \, \text{Å}$) BCS superconductors. In this case, a strong correlation between the electrons plays a significant role in the superconductivity of InN. At present we consider that the superconductivity is caused by the anomalous electron distribution in the $ab$ plane. When InN does not show superconductivity, it has a special electronic band spread in the $ab$ plane [7]. In this case, when the temperature is higher than 40 K, the electrons belonging to $B$ can migrate freely in the conduction band. Below 40 K, the localization becomes obvious and then below 3 K, the electrons travelling along $[10\overline{1}0]$ localize strongly. When InN shows superconductivity, it has glassy-vortex solid and its superconducting current is tunnelling through micro Josephson-junctions mainly in the $ab$ plane [20]. In either case, most of the InN remains in a normal, or semiconductor condition, indicating that the superconductivity of InN should be considered as a “superconductivity of a disorder-induced indium thin-film”.

Previously, we investigated the stability of the structure of InN using a first principle molecular dynamical calculation so as to reproduce the phonon density of states of InN [23]. The structure was traced every $2 \times 10^{-15} \, \text{s}$, a polarity reversal (inversion domain) was often observed in the $4 \times 4 \times 4$ unit cells due to the weak force constants along the $c$-axis. The $u$-parameter was, therefore, not determined uniquely. Such a polarity reversal is not observed in GaN. When it occurs, In atoms exchange their positions with $N$ atoms and In–In chains with a bond length of 2.14 Å ($u = \frac{1}{4}$) are produced along $[1 \overline{1} 2 0]$. These features are shown in Fig. 5, where $P$ and $Q$ are indium atoms replacing nitrogen atoms. The observed In–In chains are similar to a monolayer of In deposited onto a clean Si(111) surface, where In$(4 \times 1)$ reconstruction is observed [24]. The direction of the In chain is $[\overline{1} 1 \overline{0}]$ with a bond length of 2.88 Å [25]. The chain has three metallic bands and charge-density-wave instability at low temperature [26]. We suggest that the InN investigated here must contain In–In chains spread in the $ab$ plane with the direction $[1 \overline{1} 2 0]$. When the chains are longer than the coherent length, InN becomes a superconductor with micro Josephson-junctions. If the length is shorter, an electronic band with clear SdH signals ($k_F \sim 5 \times 10^8 \, \text{m}^{-1}$) is observed.

**5. Conclusion**

We have presented superconductivity data from a number of InN samples with different carrier densities. There is an optimum carrier density for the occurrence of superconductivity and the lower limit is determined by Mott transition and the upper limit by superconductor to
insulator transition. We propose a mechanism for the superconductivity which involves superconducting In–In chains, caused by the inversion domains and spreading throughout the ab plane.

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