

Superconductivity of InN

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The crystal structure of InN is wurtzite and its interplanar spacing of $(10\overline{1}1)$ is almost the same as that of tetragonal In(101). The crystallographic similarity produces many problems to solve about the electronic properties of semiconducting InN. Above all, there is a controversy over the possibility that In layers in InN that contains poly-crystalline phase couple by tunneling and exhibit no substantial depression of their superconducting transition temperature from the bulk In value. Here we present a superconductor to insulator transition in highly disordered InN with grains having a $(10\overline{1}1)$ plane parallel to sapphire (0001).

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1 Introduction

When we reported our observation of superconductivity of InN in 2000 for the first time, we did not discuss its mechanism because we could not regard the superconductivity as a fundamental property of InN [1]. At that time it was well known that crystal growth of InN was very difficult and a minor change of the growth condition would easily produce a metal–In droplet in InN. In the succeeding experiments, however, we made clear that neither metal–In films nor the involvement of metal–In droplets were the cause of the superconductivity [2]. We then considered that there was an optimum carrier density for the occurrence of the superconductivity. The scenario was as follows: when the lattice imperfection becomes large enough, but not too large, to produce high carrier density, a metal–In network would form in InN and produce a clear Fermi surface of a degenerate semiconductor, the superconductivity vanishes [3]. This scenario, however, was found to be wrong in the recent experiments done at Grenoble High Magnetic Field Lab., where InN films with a clear Fermi surface became superconductors [4].

Still, it is obvious that InN with a small carrier density and with a well-defined Fermi surface shows superconductivity, and that neither the electron density nor the crystal quality is the main cause of the superconductivity. We also know that the superconductivity is of the second kind and that the uppercritical field determined from the magnetic field dependence of zero-resistance temperature is a crossover from glassy-vortex lattice to liquid-vortex phases due to the thermal and quantum fluctuations of the vortex, which suggests that the coherent length is short and the penetration length is long. Neither the surface electron accumulation layer nor the metal–In precipitation has any contribution to the superconductivity.

Recently it was reported that the XRD diffraction feature at $2\theta \approx 33^{\circ}$, which had been attributed to metal In(101), i.e., the presence of metallic In clusters, was found to be an InN(1011) Bragg spot. Maleyre et al. showed that MOCVD grown powdered InN did not contain a metal In droplet and that the Bragg intensity of (1011) was similar to that of (0002) [5]. Yu et al. made clear that InN grown directly

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on a sapphire substrate without buffer layers involved a polycrystalline phase and that a (1011) spot was observed at 33° [6]. The spot at 33° is often observed in MOCVD grown InN, and we used it in the previous papers as an index of the crystal degradation, where the superconducting transition temperature T_c showed no relation to the intensity ratio of In(101)/InN(0002). If we regard this spot as an index of the involvement of the polycrystalline phase or disorder in InN, we will have a new understanding of the

At present it is not easy to evaluate the involvement of disorder in the InN with high mobility and low carrier concentration and hence it is difficult to determine its contribution to the occurrence of the superconductivity in such InN. On the other hand, when the InN contains disorder as a poly-crystalline phase, the magnitude of disorder can be evaluated by detecting the intensity of the (1011) reflection. Hence in this report we present the relationship between the superconducting resistivity change and the involvement of polycrystalline phase using the InN with high carrier concentration, and propose a possible mechanism of the superconductivity of InN, assuming In layers coupled by tunneling, and exhibiting no substantial depression of their superconducting transition temperature from the bulk value.

2 Experimental details

physical properties of superconducting InN.

InN films were grown on sapphire (0001) substrates using a conventional MOCVD method. The growth temperature was 600 to 615 °C, the reaction pressure was 600 Torr, and the source gases were NH₃ and TMI. Nitrogen was used as the carrier gas. The growth of InN on sapphire was preceded by 10 min of nitridation at 1000 °C under an NH₃ flow rate of 1000 sccm. The grown film thickness was ~350 nm. The obtained InN had a mobility (μ_e) from 30 to 100 cm² V⁻¹ s⁻¹ and a carrier density (n_e) from 3×10^{20} cm⁻³ to 7×10^{20} cm⁻³. The InN films had a hexagonal structure with its *c*-axis perpendicular to the sapphire (0001) plane. The orientation of InN [1210] was parallel to Al₂O₃ [1010]. The sample conditions are listed in Table 1. The samples were cooled to 0.5 K in a ³He cryostat equipped with a 15 T superconducting magnet. The magnetoresistance was measured as a function of field B and the angle between the direction of B and the crystal *c*-axis. The resistance of the samples was measured by a conventional dc 4-probe method. The measurement current along [1010] was 0.1 mA.

In this experiment we used two types of buffer layers; one was an amorphous double-buffer layer of 10 nm-thick InN and 10 nm-thick GaN grown at 550 °C on nitrided sapphire (0001) (no. 680, no. 692), and the other was a crystalline buffer layer grown at 600 °C (no. 753, no. 757).

High-resolution X-ray diffraction and reciprocal space mapping were performed using a Philips high resolution diffractometer with Cu K α_1 radiation. The samples investigated had InN(1011) reflection. As is given in the previous report [7], when the sample has a strong (1011) reflection, the reciprocal space mapping of (1011) is round and isolated, indicating that there are grains or involvement of a secondary phase in InN with their c axis tilted so that (1011) is parallel to the sapphire (0001) plane (denoted as (1011) grain). The degree of the grain involvement was estimated from the X-ray Bragg intensity ratio of InN(1011) to Al₂O₃(0002), which is given in Table 1. The difference between no. 753 and no. 757 and between no. 692 and no. 680 are their growth temperatures. As is seen in Table 1, a slight difference in growth temperature affects the electrical characteristics considerably, especially superconducting properties.

Table 1 Summary of sample conditions. Growth temperature is given by T_s . Involvement of grains with the InN(1011) plane parallel to sapphire (0001) is estimated by the X-ray intensity ratio of InN(1011)/Al₂O₃(0006).

sample	680	692	753	757	
$T_{\rm s}$ (°C)	613	616	613	610	
$n_{\rm e} (10^{20}{\rm cm}^{-3})$	2.9	4.6	4.5	6.8	
$\mu_{\rm e} ({\rm cm}^2{ m V}^{-1}{ m s}^{-1})$	102	57	66	28	
$InN(10\overline{1}1)/Al_2O_3(0006) (\times 10^{-3})$	4.3	2.1	0.5	0.6	

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Fig. 1 (online colour at: www.pss-a.com) XRD measurements of the InN films in $\theta - 2\theta$ configuration. Peaks at $2\theta = 31.56^{\circ}$ are InN(0002), $\approx 33.10^{\circ}$ InN(1011), and $\approx 34.8^{\circ}$ the GaN(0002) buffer layer.

3 Results and discussion

Figure 1 shows the XRD scan of the samples investigated. Samples no. 680 and no. 692 do not have crystalline buffer layers, and therefore they have a clear $InN(10\overline{1}1)$ reflection around 33°. Judging from the intensity ratio of $InN(10\overline{1}1)$ to sapphire (0006), no. 680 contains the highest amount of (1011) grains. Samples no. 753 and 757 also have a broad peak around 33°, but their intensity ratios are lower than those of the samples with amorphous buffer layers. Sample no. 753 has the lowest amount of (1011) grain.

Figure 2 shows the temperature dependence of the resistivity of the samples shown in Fig. 1. The vertical scale is normalized by the resistivity at 4.2 K. All of the samples show a resistivity anomaly around 3.4 K, which is the superconducting transition temperature of bulk In. Sample no. 680 changes into an insulator. Previously we reported that InN with a carrier density of 1.8×10^{18} cm⁻³ showed insulating behavior due to the carrier localization [8]. As for sample no. 680, its resistivity increases below 3.4 K and the ratio of the resistivity change below 3.4 K is more than one order of magnitude higher than that observed in InN with the carrier localization. Sample no. 692, whose n_e is similar to that of no. 680, starts to show a small resistivity decrease at 3.4 K, and shows superconducting transition at 1.5 K and reaches zero resistance at 0.5 K. As for InN with a crystalline buffer layer, it shows a clear superconducting transition at 3.4 K. When a sample contains more ($10\overline{11}$) grains (no. 757), its transition starts at 3.4 K, which is very steep and clear. On the other hand, no. 753 starts to show a gradual decrease of resistance at 1.8 K, the same as no. 757.

Figure 3 shows the magnetoresistance of the four samples at 0.5 K at $B \perp ab$ -plane. Melting field of the glassy-vortex solid of InN (resistance vanishing field) is 0.3 T for no. 753, 0.2 T for no. 757 and



Fig. 2 (online colour at: www.pss-a.com) Temperatur dependence of the resistivity of InN. The vertical scale is normalized by the value at 4.2 K.



Fig. 3 (online colour at: www.pss-a.com) Magnetic field dependence of the resistivity of InN. The vertical scale is normalized by the value at 4.2 K. The field is applied perpendicular to the *ab*-plane and to the current.

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0.01 T for no. 692, much larger values than 0.023 T, the critical field of metal In, which is a type I superconductor. The resistivity of no. 680 returns to its initial value at B = 0.3 T. The magnetic field dependence of the resistivity is similar to that observed in the temperature dependence of the resistivity shown in Fig. 2. Hence it can be said that the resistivity anomaly of no. 680 originates in the superconductivity of InN and that a superconductor-insulator transition occurs at 3.4 K.

Since P. W. Anderson predicted the behavior of the superconductivity of disordered metallic systems, where localization did not have a significant contribution to the BCS superconductivity in dirty metals, but reduced the T_c and finally changed the superconductor into insulator [9], the superconductorinsulator transition has been extensively studied in various systems. Disordered metal-In films have been investigated as a good candidate to understand this mechanism, and the transition is understood as the metal In films being coupled by Josephson junction, exhibiting no substantial depression of their superconducting transition mechanism from the bulk In [10]. When InN has a carrier concentration lower than 10^{18} cm⁻³ and shows superocnducting transition, its resistivity change is smooth as is observed in no. 753, though it occurs at lower temperatures [4]. When the disorder (involvement of (1011) grains) increases (no. 757), the temperature of the resistivity change increases to 3.4 K and the change is not so smooth as in no. 753 because of the trapping of the Cooper-pairs. When the disorder becomes even stronger, the Cooper-pairs produced by the superconductiving transition are trapped by the disorder more strongly (no. 692), and finally, InN changes into an insulator, where the Cooper-pairs are localized by the strong disorder in InN. When the field is applied, the Cooper-pairs are more easily dissolved into electrons and the resistivity returns to its initial value in reverse, from no. 680 to no. 753 as is seen in Fig. 3. The superconductivity of InN, therefore, is very sensitive to the presence of the $(10\overline{1}1)$ grains within.

The interplanar spacing of $InN(10\overline{1}1)$ is 2.704 Å and that of metal In(101) is 2.712 Å at room temperature. According to Paszkowicz et al., the spacing of In(101) becomes 2.706 Å at 105 K [11], so both spacings are almost the same. As was reported before, InN has a very sharp lower E_2 phonon at 87 cm⁻¹, which indicates that the out-of-phase vibration of In atoms parallel to sapphire (0001) has a long lifetime even when n_e is larger than 10^{20} cm⁻³ [1]. Moreover, the A₁ (LO) phonon and free carriers in InN couple non-linearly, where Fano interference between the zone-center LO phonon and quasicontinuum electronic state along *c*-axis is prominent [12]. Judging from these results, when the grains having a (1011) plane parallel to sapphire (0001) are involved, the crystal structure of InN is regarded as having a twodimensional In-layer structure intercalated by nitrogen layers along $[10\overline{1}1]$, or along *c*-axis. The localization anisotropy observed in the *ab*-plane [8] is an evidence to support this consideration. If it is so, we can understand the superconductivity of InN in terms of the metal In layers coupled by Josephson junction along [1011]. In this case the carrier density of InN has no relation to the superconducting transition. When the disorder becomes stronger, or the involvement of grains becomes larger, the Cooper-pairs are localized and finally InN changes into an insulator. In this scenario the carrier concentration is the measure of the disorder and we do not need to consider the contribution of the In-droplet to the occurrence of the superconductivity.

4 Conclusion

We reported that there is a superconductor to insulator transition in highly disordered InN. From the relationship between the superconductivity and the involvement of $(10\overline{1}1)$ grains, we suggested that when the grains having a $(10\overline{1}1)$ plane parallel to sapphire (0001) are involved, the crystal structure of InN is regarded as having a two-dimensional In-layer structure intercalated by nitrogen layers along $[10\overline{1}1]$, or along *c*-axis because the interplanar spacing of InN $(10\overline{1}1)$ is almost the same as that of metal In(101). It may be concluded that the superconductivity of InN is caused by the metal In layers coupled by Josephson junction along $[10\overline{1}1]$.

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References

- T. Inushima, V. V. Mamutin, V. A. Vekshin, S. V. Ivanov, T. Sakon, S. Motokawa, and S. Ohoya, J. Cryst. Growth 227–228, 481 (2001).
- [2] T. Inushima, T. Takenobu, M. Motokawa, K. Koide, A. Hashimoto, A. Yamamoto, Y. Saito, T. Yamaguchi, and Y. Nanishi, phys. stat. sol. (c) 0, 364 (2002).
- [3] T. Inushima, N. Kato, Y. Sasaki, T. Takenobu, and M. Motokawa, phys. stat. sol. (c) 2, 2271 (2005).
- [4] T. Inushima, N. Kato, D. K. Maude, Hai Lu, W. J. Schaff, R. Tauk, Y. Meziani, S. Ruffenack, O. Briot, W. Knap, B. Gil, H. Miwa, A. Yamamoto, D. Muto, Y. Nanishi, H. Higashiwaki, and T. Matsui, in: Proceedings of the 6th Int. Conf. of Nitride Semiconductors (Bremen, 2005).
- [5] B. Maleyre, S. Ruffenach, O. Briot, and A. van der Lee, Superlattices Microstruct. 36, 527 (2004).
- [6] K. M. Yu, Z. Liliental-Weber, W. Walukiewicz, W. Shan, J. W. Ager III, S. X. Li, R. E. Jones, E. E. Haller, H. Lu, and W. J. Schaff, Appl. Phys. Lett. 86, 071910 (2005).
- [7] T. Inushima, T. Takenobu, M. Motokawa, K. Koide, A. Hashimoto, A. Yamamoto, Y. Sato, T. Yamaguchi, and Y. Nanishi, Physik Mikrostrukturierter Halbleiter 27, 131 (2002).
- [8] T. Inushima, M. Higashiwaki, T. Matsui, T. Takenobu, and M. Motokawa, Phys. Rev. B 72, 085210 (2005).
- [9] P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
- [10] S. Okuma and N. Kokubo, Phys. Rev. B 51, 15415 (1995).
- [11] W. Paszkowicz, R. Cerny, and S. Krukowski, Powder Diffr. 18, 114 (2003).
- [12] T. Inushima, M. Higashiwaki, and T. Matsui, Phys. Rev. B 68, 235204 (2003).