Superconductivity and mixed-state characteristic of InN films by metal-organic vapor phase epitaxy

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Abstract

We have performed resistivity, magneto-resistance and Hall resistance measurements on metal-organic vapor phase epitaxy (MOCVD) grown InN films on Si substrate. Superconducting phase transition and anomalous mixed-state behavior were observed in wurtzite-structured InN thin films. The resistance is metallic like over a wide temperature range ($4\text{ K} \leq T \leq 300\text{ K}$) and $R(300\text{ K})/R(4\text{ K})$ is about 1.1. The carrier concentration and mobility measurements show the InN thin films in this range a degenerate electronics system. However, the resistivity starts to change at 4 K, which makes the slope of the temperature dependence larger at 1.5 K. Then it become less than 10^{-3} at 0.3 K. The films show positive magnetoresistance (PMR) between 0.3 and 4 K at $B_{\parallel}$ ($B \parallel c$ -axis of InN) $< 0.8\text{ T}$. The PMR can be understood as superconductor mixed state behavior and origin from the flux dynamics. We measured Hall coefficients of InN thin films in the superconducting mixed states. Anomalous Hall effects were observed at 0.3 K. There is no Shubnikov-de Haas (SdH) oscillations observed until B is 15 T. Details are discussed in the paper. © 2006 Elsevier B.V. All rights reserved.

Keywords: InN; Superconductivity; Mixed state

InN, a promising candidate for the high mobility electronics and a wide range of optoelectronic devices, such as laser diode, light-emitting diodes, solar cells, IR detectors, THz emitters, has been attracting a great deal of interest recently [1–4]. However, this material suffers from the lack of a suitable substrate and large disparity of the atomic radii of In and N, which cause high native defect concentrations in it. The native defect responsible for naturally occurring n-type InN is nitrogen vacancy [5]. More recently, the superconductivity of InN ($T_c \sim 2\text{ K}$) with carrier concentration of $2 \times 10^{20}\text{ cm}^{-3}$ and mobility of $132\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ was reported by Inushima [6]. They demonstrated that the superconductivity of InN is of the second kind and is anisotropic. Moreover, they also showed that T_c of InN, with lower carrier concentration of $5 \times 10^{17}\text{ cm}^{-3}$, reduced to 0.1 K. A model of electron density dependence of electronic structure of InN, which is considered to be due to the contribution of the core d electrons of In atoms, was proposed [3]. For stabilizing the crystal structure of InN, the 4d-semicore electrons of In overlap largely with the valence states of InN [7]. The strong spin–orbit interaction

of InN is suggested due to the 4d-semicore electrons mixing at the top of the valence band [7,8].

Superconductivity in degenerate semiconductors is an interesting issue for both theory and experiment. Such carrier density dependence of T_c has been reported for heavily boron-doped diamond thin films and was explained in the framework of electron-phonon coupling of the same type as in MgB_2 , but in three dimensions [9–11]. The coupling strength is as function of hole-doping. The superconductivity is type II and isotropic. This is quite different from naturally n-type InN. The mechanism of superconductivity in unintentionally doped n-type InN remains unclear. Despite the intense study was made, experimental investigations of superconducting mixed state properties in InN system are minuscule.

For wurtzite-structured InN epitaxial layers grown on different substrates, there are two kinds of polarities, which are In-face and N-face for GaN buffer layer without nitridation and high-temperature nitridation of substrate, respectively [12]. The experimental results proposed by Inushima was based on the high-temperature nitridation of substrate and has N-face InN thin films [6]. To make clear the superconducting mechanism in InN, the experimental measurement of the other polarity of In-face is important. Here we report the

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Fig. 1. (a) The configuration of InN thin films on GaN/Si and GaN/sapphire substrates. The thickness of InN thin film is 260 nm. (b) The Raman spectrum of InN thin film on GaN/Si and GaN/sapphire substrates and demonstrated high-quality wurtzite-structured epitaxial layer obtained on both substrates with GaN buffer layers.

experimental results of InN thin film on GaN buffer layers with In-face.

The InN samples used in this study were grown by an Aixtron 200/4RF-S metal-organic vapor phase epitaxy (MOVPE) system on GaN buffer layers. Fig. 1(a) and (b) shows the structure of InN thin film on Si and sapphire substrates, respectively. A 250 nm-thick buffer layer was deposited at 720 °C on Si substrate, followed by the growth of an approximately 0.5 μm-thick GaN at 1050 °C. The growth temperature for InN is in the range of 550 °C. The phonon structure of InN thin film was determined by Raman analysis. The structure and Raman analysis of InN thin film on sapphire are for comparison with that of InN on Si substrate as shown in Fig. 1(a) and (b). Fig. 1(b) is the Raman analysis of these two samples. The full width at half maximum (FWHM) of the $E_2^{(2)}$ mode in the symmetry of the Raman shifts can represent thin film quality. The Raman analysis shows that high-quality wurtzite-structured epitaxial layers formed with their *c*-spacing perpendicular to the substrate surface. The details of the growth process are described elsewhere [13,14].

The temperature dependence of the resistivity, mobility and carrier concentration were measured by using a continuous-flow He4 cryostat when $T > 4$ K and He³ cryostat when $T < 4$ K. All the electrical transport measurements were performed on cleaved

squares (2–3 mm) on a side. Four-terminal transport measurements were used in our system. Al or Au electrodes on the samples were connected to the outer electrodes by conductive silver paste. The metal such as Au, Ti, Al and Ni can always form an ohmic contact on InN thin film without any annealing required [15]. The electron densities and resistivity were determined by Hall measurements with van der Pauw geometry. The samples were slowly drifted in temperature over several hours and data were taken in a rapid succession (≈ 1 s). Results are presented in Fig. 2(a), (b) and (c). Fig. 2(a) shows the measured resistivity as a function of temperature at $4 \text{ K} < T < 300 \text{ K}$. We can see that the resistivity decreases as the temperature decreases and the ratio ρ_{RT}/ρ_{5K} is about 1.09, which present a metallic behavior. Fig. 2(b) shows the measured mobility as a function of temperature. The mobility is $658 \text{ cm}^2/\text{Vs}$ at 285 K and become $720 \text{ cm}^2/\text{Vs}$ at 5 K. The mobility decreases with increasing temperature when $T > 150 \text{ K}$. However, there is small increasing mobility with increasing temperature when $T < 150 \text{ K}$. Fig. 2(c) shows the measured carrier density n as a function of temperature. The carrier concentration is about $1.6 \times 10^{19} \text{ cm}^{-3}$ and has been approximately temperature-independent. Therefore, InN film on GaN/Si substrate could be considered as degenerate electron systems in which the Fermi level is much higher than the conduction-band minimum [15,17,18].

Fig. 2. (a) The measured resistivity ρ as a function of temperature T for InN on Si. (b) The measured mobilities μ as a function of temperature T for InN on Si. (c) The measured carrier concentration n as a function of temperature T for InN on Si.

Fig. 3 shows the measured resistance as a function of temperature at $T < 4.2 \text{ K}$. The resistance of InN thin film on GaN/Si substrate starts to fall rapidly at 4 K ($R_{4\text{K}}/R_{2.5\text{K}} \sim 1.2$), which makes the slope of the temperature dependence larger at 1.5 K, and then become less than 10^{-3} at 0.3 K. This result can

Fig. 3. The electrical resistance R as a function of temperature T . The resistance starts to fall rapidly at 4 K ($R_{4\text{K}}/R_{2.5\text{K}} \sim 1.2$), which makes the slope of the temperature dependence larger at 1.5 K, and then become less than 10^{-3} at 0.3 K.

rule out the possibility that the superconductivity of InN thin film results from the In droplets on the surface of the samples or the In segregation at columnar boundaries, where a drastic change of resistivity should be found at 3.4 K instead of 4 K [19]. Moreover, the structure quality of the thin film revealed by Raman spectrum demonstrated the absence of any Raman shifts of such developed In-enriched network. Therefore, our results suggest that the superconducting phase in this system is due to the InN compound.

Superconductivity of the type two exists mixed states of superconducting state and normal-metal state at appropriate temperature and magnetic field. Fig. 4 shows the field-dependence of magneto-resistance between 0.3 and 4 K at $B_{\parallel}$ ($B \parallel c$ -axis of InN) $< 0.8 \text{ T}$. It shows positive magneto-resistance (PMR) when $|B_{\parallel}| < 0.8 \text{ T}$ at $0.3 \text{ K} < T < 4 \text{ K}$. The PMR in superconducting mixed states can be explained in terms of flux dynamics [20,21]. The flux flow in mixed states will induce a electric field in the sample according to the equation, $E_{\text{ind}} = B \times V_L / c$, where B is magnetic field, c is the speed of light, V_L is the velocity of magnetic flux vortex and E_{ind} is the

Fig. 4. The measured magneto-resistance as a function of magnetic field at $0.3 \text{ K} < T < 4.2 \text{ K}$.

Fig. 5. (a) The measured Hall coefficient $R_{xy}(T)$ as a function of magnetic field at $T=10$ and $0.3 K$, respectively for InN on sapphire substrate. The Hall sign changes from negative to positive when B is $0.026 T$ at $0.3 K$. (b). The measured Hall coefficient $R_{xy}(T)$ as a function of magnetic field $B(T)$ at $T=0.3 K$ for InN on Si substrate. The slope of Hall coefficient vs. B changes from negative to positive when B is $0.06 T$ at $0.3 K$.

induced electric field. Therefore, the magneto-resistance increases with increasing magnetic field at fixed temperature. There is no SdH oscillation, which is always observed in 2-DEG system, until B is $15 T$ in this system.

In order to realize effect of carrier type in the superconducting mechanism of degenerate semiconductors, it is important to understand this property in mixed state of InN system. The Hall sign of R_{xy} , $R_{xy} = \frac{B}{ned}$, where n is carrier concentration and d is the thickness of InN thin film, represents the carrier type. Anomalous Hall coefficient, where the Hall sign changes from negative to positive, was first observed in InN. Fig. 5(a) shows the measured Hall coefficient $R_{xy}(T)$ as a function of magnetic field at $T=10$ and $0.3 K$, respectively for InN on sapphire. Unlike constant slope at $10 K$, the Hall sign changes from negative to positive when B is $0.026 T$ at $0.3 K$. Fig. 5(b) shows the measured Hall coefficient $R_{xy}(T)$ as a function of magnetic field at $0.3 K$ for InN on Si. Anomalous Hall effect, where the slope of Hall coefficient vs. B changes

from negative to positive when B is $0.06 T$ at $0.3 K$, was observed. The behavior was quite different from that of InN on sapphire substrate and might be due to the much more complicated electronic structure caused by the lattice mismatch between InN and Si substrate. The Hall sign anomaly was observed both in high temperature superconductors [15,16] and was explained in terms of flux dynamics in CuO-plane of $YBa_2Cu_3O_{7-\delta}$ system. Lots of experimental works have shown that the Hall anomaly occurs in both p-type superconductors, such as $YBa_2Cu_3O_{7-\delta}$ system and n-type superconductors, such as $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ system. The superconductivity is of type II and anisotropic. Superconducting mechanism of these systems is related to d -electrons in these materials.

It is known that InN possesses superior transport properties to those of III-nitride semiconductors over a wide temperature range [17]. The superconductivity in wurtzite-structured InN suggests that GaN, which form also in wurtzite-structured III–V semiconductors, may similarly exhibit superconductivity under the appropriate conditions.

In conclusion, we have performed transport measurements on InN thin films over a wide temperature range. Different polarity with In-face of InN was studied. Superconducting phase transition and anomalous mixed-state behavior were observed in this work. The resistance is metallic like over a wide temperature range ($4 K \leq T \leq 285 K$) and the R_{RT}/R_{4K} is about 1.09. The carrier concentration and mobility measurements show the InN thin films on Si substrate in this range a degenerate electronics system. The resistance shows anomaly at $4 K$ ($R_{4K}/R_{2.5K} \sim 1.2$), which makes the slope of the temperature dependence larger at $1.5 K$, and then become less than 10^{-3} at $0.3 K$. The films show positive magneto-resistance when $B_{||} < 0.8 T$ at $T < 4 K$. Anomalous Hall coefficient was observed in InN.

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