Electrical and optical properties of InN with periodic metallic In insertions

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We report on a growth by molecular beam epitaxy of InN:In semiconductor/metal composite structures containing periodically inserted arrays of In clusters formed by intentional deposition of In metal films in a thickness range of 2−48 monolayers. It was found that indium insertions do not change markedly carrier mobility in the composites, that remains in the 1300−1600 $cm^2/(V\cdot s)$ range, while carrier concentration increases with rising In amount. Spectra of thermally detected optical absorption do not exhibit a noticeable Burstein−Moss shift of a principal absorption edge with increasing the carrier concentration, but rather complicated modification of their shapes.

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InN is a material attracting a lot of attention today due to potential device applications. Indium nitride was predicted to have the lowest effective mass of electrons among III-nitrides. This may results in high values of carrier mobility and saturation velocity, making InN a promising material for the fabrication of high performance high electron mobility transistors, high frequency devices, full-spectrum solar cells [1–3]. The transport parameters of InN almost do not depend on temperature and doping concentration that suggests that InN may have distinct advantages being used in high frequency centimeter and millimeter wave devices. Another possible application of InN is fabrication of high-speed laser diodes and photodiodes in the optical communication system, although for such devices InN films with p-type of conductivity are necessary. However, sufficient p-type is not realized in InN due to high background donors concentration [1,4,5]. Recent progress in growth techniques has led to fabrication of InN films of improved crystal quality [6]. Nevertheless, in general, the values of carrier concentration n in InN have been still remaining high enough. For films grown by metal-organic chemical vapor deposition (MOVPE) n varies from $\sim 5\cdot 10^{18}$ to $\sim 3\cdot 10^{19}\,cm^{-3}$ [7], and for molecular beam epitaxial (MBE) InN $n = 2.8\cdot 10^{17}-10^{20}\,cm^{-3}$ [8,9], although the lowest value has been calculated, taking account of an existence of a surface carrier accumalation layer. Values of the carrier mobility μ also vary in the wide range — from several hundreds to more than 2000 $cm^2/(V\cdot s)$ for both MOVPE and MBE grown InN films [7–9], reaching the maximum value of 2370 $cm^2/(V\cdot s)$ in an MBE grown film [9]. A strong dependence of n and μ on layers thickness d was also observed [10,11], the best values being reported for layers with d much greater than 1 μm [9]. One should note however that the highest electron mobility observed in InN is noticeably smaller than the theoretically predicted value [12], that makes improvement of elelctrical properties of InN an insistent demand.

The accurate data on the carrier concentration are necessary to design any of InN-based devices, as well as to determine the fundamental band gap, E_g, from experimental data taking into account possible Burstein−Moss effect. It is worth noting that a Burstein−Moss shift of an effective absorption edge in InN films is assumed to be abnormally high (~ 1 eV) [13,14]. In all other $A^{III}B^{V}$ semiconductors, the value of the shift does not exceed 0.1−0.2 eV due to the effect of potential fluctuations induced by randomly distributed charged defects [15]. Therefore we assume that more realistic description of the InN absorption edge behavior should include additionally effects of In clustering, nonstoichiometry and compensation [16]. Among them, the In clustering is the most serious problem resulting frequently in deposition of a semiconductor/metal composite instead of an ideal semiconductor compound. The clusters appear because InN has a small heat of formation [17] and, hence, can easily dissociate at typical growth temperatures. During growth at the substrate temperature usually below 550°C for N-polar surface (450°C for In-polar surface [18]) and nearly $N/In = 1:1$ conditions the low In vapor pressure over the accidentally arisen In metal phase prevents its evaporation from the surface [19]. Weak In−N bond, as compared to In−In and especially N−N bonds, further promotes formation of In clusters even in the bulk. The statistical distribution of the cluster sizes is controlled by growth regimes [20].

Recently, it has been shown that such In inclusions can influence a spatial distribution of infrared luminescence and induce additional absorption within InN [21]. Generally, such absorption may have two components which are

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superimposed with the InN absorption and, hence, mask it. One of them is related to the Mie resonances, which appear when size of In clusters is large enough to maintain plasmonic excitations without significant scattering at boundaries. The other mechanism is inter-parallel band absorption in metallic indium. In accordance with theoretical estimation, it has two maximum — one at 0.6–0.7ėV and the other at 1.5 eV [22,23]. Thus the onset of this absorption is very close to the generally accepted band gap of InN. One can assume that the metallic clusters should affect the carrier concentration and mobility in InN as well. However to the best of our knowledge, no such investigations have been reported yet.

In this paper we report on a study of electrical and optical properties of InN films with intentionally introduced periodic plane arrays of In clusters. This approach provides a useful tool to follow electrical and optical properties of InN epilayers possessing different well-controlled amount of incorporated metallic indium. We demonstrate a weak deviation of basic electrical parameters in such composites with respect to data reported for conventional InN films. We show also a weak dependence of absorption onset on carrier concentration in such structures.

Semiconductor/metal composite structures InN:In were grown by plasma-assisted molecular beam epitaxy (PA MBE) on c-Al_2O_3 substrates on top of GaN and InN buffer layers that presumably ensure the N-polarity of the films. A Compact 21 T (RIBER) PA MBE setup was equipped with an HD-25 OAR plasma source. The growth temperature was kept constant at 480°C. Depending on the N/In flux ratio used, this PA MBE technique permits us to grow InN films with intense photoluminescence (PL) at ~ 0.7 eV, carrier concentration $n \approx 2 \cdot 10^{18}–2 \cdot 10^{19}\,\text{cm}^{-3}$, and carrier mobility up to $\mu \approx 1800\,\text{cm}^2/(\text{V}\cdot\text{s})$ achieved at nearly $\text{N/In} = 1:1$ in ~ 1-μm-thick layers. The investigated structures were fabricated by periodic deposition of pure In metallic insertions and 25-nm-thick InN binary layers. The exposure time of In t_{In} varied from 5 to 120 s for different samples, that approximately corresponds to variation of In nominal layer thickness d_{In} in the range from 2 monolayers (ML) (0.6 nm) to 48 ML (14.4 nm). The number of the In insertions was 20, except for the 48 ML structure, where growth was terminated after 6 periods due to growth surface disturbance reflected in a decay of the streaky reflection high energy electron diffraction (RHEED) pattern. All other structures demonstrated till the end of growth process a 2D streaky RHEED pattern typically observed during InN growth under optimum conditions [14]. As a result, we have grown InN:In composite periodic structures, in which the total thickness equals to $\sim 300–600$ nm and comprises nominally up to 1/3 of the metallic In insertions. All InN interlayers were grown under slightly N-rich conditions to suppress spontaneous formation of In clusters during growth. A conventional InN film without insertions was also grown under the same conditions for a reference. Intense enough photoluminescence and cathodoluminescence was observed in all the structures and will be published elsewhere.

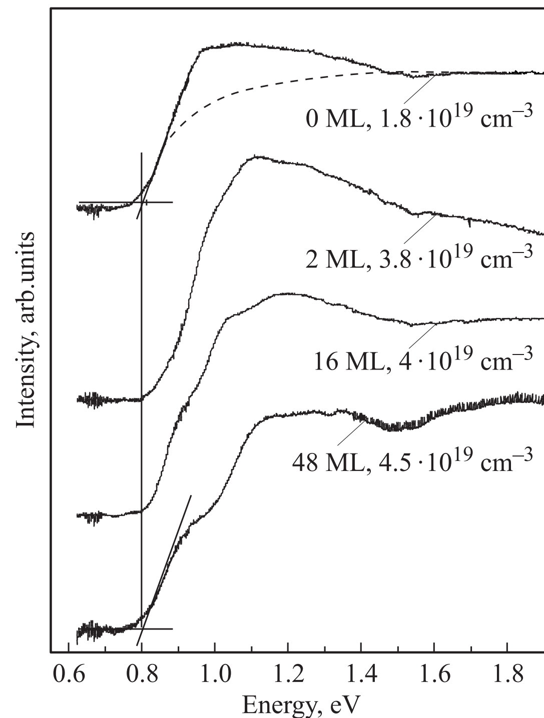

Fig. 1. Selected spectra of thermally detected optical absorption recorded in the samples with different In insertions (the reflection is taken into account). The measured carrier concentration and the nominal thickness of the insertions are marked in the plot. The dashed line presents calculated dependence for conventional semiconductor.

Measurements of the Hall coefficient R_{H} and resistivity ρ were performed in the Van der Pauw geometry at temperatures 77–300 K, using a 0.06 T magnetic field. Electric contacts were soldered with In to square-shaped samples. Thermally detected optical absorption (TDOA) measurements were performed at 0.35 K in a pumped 3 He cryostat. The sapphire substrate is characterized by a high thermal conductivity that provides good thermal contact of a studied layer with a Ge thermoresistor mounted on its back side. A narrow-gap (~ 0.2 eV) InSb bolometer was used to obtain a reference sighnal. Both sample and bolometer were excited simultaneously by a light of a tungsten lamp, passing through a JOBIN-YVON monochromator. This TDOA study is complemented by measurements of the conventional optical absorption, which have demonstrated similar results [24].

The (101) In peak was observed in the Θ-2Θ X-ray diffraction scans of the InN:In structures, starting from the 8 ML In insertions. It looks reasonable because to be registered the thickness of In inclusions should exceed dozens of atomic planes. The effective value of absorption coefficient calculated for the total structure ($\alpha_{\text{eff}} \approx 10^5\,\text{cm}^{-1}$ at $E = 1.5$ eV) is higher than $\alpha \approx 5 \cdot 10^4\,\text{cm}^{-1}$ at the same energy, which has been reported for conventional InN films [25]. These facts confirm that metallic In clusters indeed are present in the investigated structures. However,

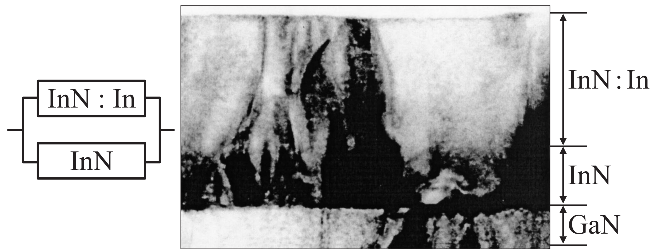

Fig. 2. TEM image ($g = 0002$) of an InN:In structure with InN:In composite film containing 8 ML In insertions. The left scheme illustrates the parallel model used for calculation.

$\alpha_{\rm eff}$ is smaller than it is expected for continuous metallic film ($\alpha \approx 10^6\,{\rm cm}^{-1}$). So, it has been concluded that the In inserts form rather arrays with chaotically distributed metallic clusters than continuous layers. It is worth mentioning that the TDOA spectrum even for the reference InN film (Fig. 1) is not consistent well with the square-root behavior on frequency ω of the imaginary part of the complex dielectric function

$$\operatorname{Im}\varepsilon(\omega) \propto \sqrt{\hbar\omega - E_{\rm g}},$$

predicted for InN as for a conventional semiconductor [26]. Thus, we assume that In nanoclusters can also arise in the reference film formed under the N-rich conditions, despite our efforts to prevent their spontaneous formation, that implies a metastable nature of the material.

A preliminary cross-section transmission electron microscopy study has shown that the InN : In structures comprise two parts (Fig. 2). One of them is pure InN buffer layer, where only the ultra-small clusters may be; the upper part is the composite film with the introduced arrays of the In clusters. In the presented image, this part looks lighter than the InN buffer due to enrichment by the heavy metal. This measurements have enabled one to distinguish the contributions of the InN buffer layer and the InN : In composite to electrical properties. We supposed that these layers are connected in parallel, and, hence, two types of conducting channels contribute to integrally measured values of $R_{\rm H}$ and ρ. We neglect of possible contribution of a surface accumulation layer. Since the InN buffer layer in the InN : In samples were grown under the same conditons as the InN reference film, one can use the electrical parameters of InN buffer to calculate carrier concentration $n_{\rm s}$ and mobility $\mu_{\rm s}$ in the InN : In composite structures.

It turns out that the Hall concentration $n_{\rm H}$ in the reference InN film and $n_{\rm s}$ in the InN : In structures do not depend on temperature in the entire temperature range (Fig. 3, *a*), that corresponds to a strongly degenerate semiconductor. The Hall mobility $\mu_{\rm H}$ in the reference film and $\mu_{\rm s}$ in the InN : In composites behave similarly with temperature (Fig. 3, *b*). In general, the μ values are limited by different scattering mechanisms — on phonons, defects and impurities. In the case of the strongly degenerate semiconductor, μ could depend on temperature only, if the main scattering mechanism is the phonon scattering. Since μ does not depend on temperature (Fig. 3, *b*), other mechanisms seem to dominate.

Furthermore, the $\mu_{\rm s}$ value does not depend on the inserted In amount, being approximately equal to $\mu_{\rm H}$ in the reference InN film at all temperatures ($1300-1600\,{\rm cm}^2/({\rm V\cdot s})$). It can be explained by the fact that due to the high surface migration velocity of In atoms, the In clusters in the sheets predominantly accumulate to defects, such as dislocations, grain boundaries, and probably some of point defects. Hence, these metal inclusions do not necessarily create the new scattering centers which may suppress $\mu_{\rm s}$ in the InN : In sturctures with respect to $\mu_{\rm H}$ in the reference InN film.

The carrier concentration $n_{\rm s}$ rises with increasing the In amount in the InN : In structures (Fig. 3, *a*), that can be associated with disturbance of crystal quality, which should lead to increasing the density of intrinsic point defects, and, consequently, to rising the carrier concentration.

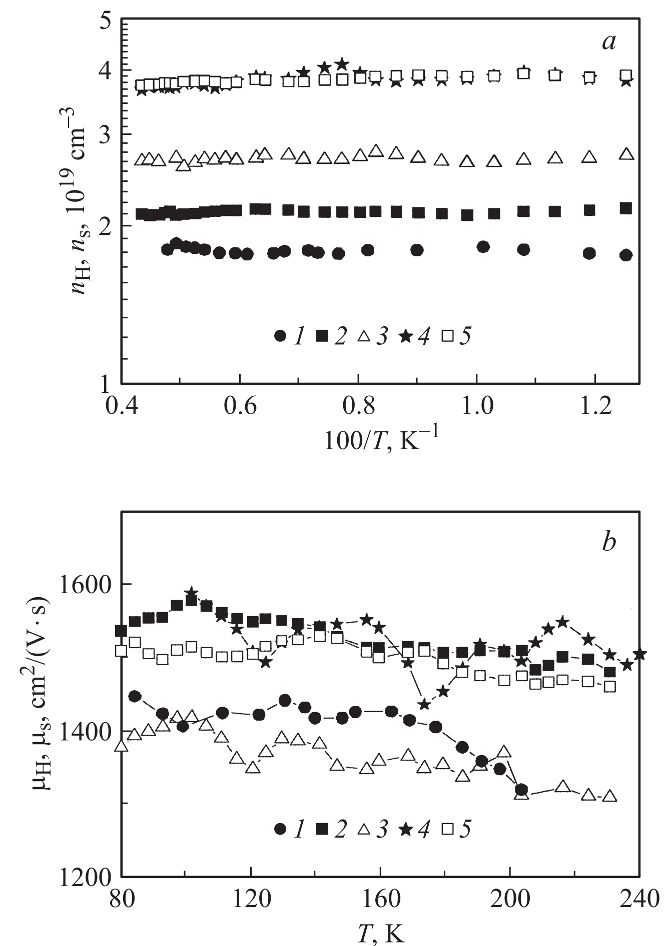

Fig. 3. *a* — temperature dependence of carrier concentration for conventional InN film $n_{\rm H}$ (*1*) and InN:In structures $n_{\rm s}$ with different nominal In thickness, ML: *2* — 2, *3* — 8, *4* — 16, *5* — 48. *b* — temperature dependence of the carrier mobility for conventional InN film $\mu_{\rm H}$ (*1*) and for InN:In structures $\mu_{\rm s}$ with different nominal In thickness, ML: *2* — 2, *3* — 8, *4* — 16, *5* — 48.

The absorption spectra in these InN:In composites demonstrate some intricate features. They have almost the same energy of the absorption onset (~ 0.8 eV), in spite of the variation of n_s from $1.8 \cdot 10^{19}$ to $4.5 \cdot 10^{19}$ cm^{-3}. Calculations done using the models presented in Refs. [13,14] shows that the Burstein–Moss shift should be of about 100–150 meV for this concentration change. One can see in Fig. 1 that the absorption spectra have complicated shapes with one or more additional peaks. We ascribe the peaks to the Mie resonances. Although the extra peaks are clearly resolved, we abstain from fitting the absorption spectra before detailed TEM characterization, which is in progress now. The onsets of the absorption may be influenced also by the inter-parallel-band transitions [22,23]. Let us underline that both these effects — the inter-parallel absorption and Mie resonances — have to be just slightly dependent on variation of the carrier concentraton in the matrix, as it has been observed experimentally.

In conclusion, we have investigated slightly N-rich InN layers with intentionally incorporated periodic arrays of metallic In clusters of well controlled amount up to 1/3 of the total structure volume. They demonstrated the values of the carrier concenration and mobility in the range of reported data on pure InN films with equivalent thickness of rather good crystal quality. The stabilization of the absorption onsets with varied carrier concentration may be indicative of the metallic cluster presence. This can be used to develop the state-of-the-art technology of InN for device applications.

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