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(Received 22 January 2008; accepted 28 February 2008; published online 17 March 2008)

We theoretically study the optical properties of the composite made of indium nitride (InN) containing metallic indium clusters, using quasistatic approximation and effective medium approximation. The influences of indium cluster shape and volume concentration on the optical properties of entire sample are systematically discussed. Our results can satisfactorily explain recent experiments on the dielectric function of InN containing indium [M. Losurdo, G. Bruno, T.-H. Kim, S. Choi, and A. Brown, Appl. Phys. Lett. **88**, 121928 (2006)]. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2898706]

Due to the weak In–N bonds, metallic indium formation is easily occurred due to indium nitride (InN) decomposition during material growth and processing.[1] As a result, compared with AlN and GaN, metallic cluster formation is a special issue which should be considered for InN related material and InN-based devices. Recently, we have demonstrated that indium can exert pronounced impact on InN growth mode, leading to the unexpected InN nanoflowers.[2] Here, we will discuss the influences of metallic indium clusters on the optical properties of InN.

Shubina *et al.*[3] have proposed that the optical absorption around 0.7 eV in InN is due to metallic indium through Mie resonances. Their paper had attracted much attention and given rise to controversy among III-nitride researchers.[4] In this paper, we will show the critical challenges faced by their viewpoints. Furthermore, we will provide a systematic theoretical guideline in understanding the optical roles of metallic indium in InN.

We first consider the situation of low indium cluster concentrations. In this case, it is reasonable to assume indium clusters are much smaller in size than the incident light wavelength $|\lambda_{vac}/\sqrt{\varepsilon_{InN}}|$ in the surrounding medium and are well separated. These assumptions mean that only the lowest-order dipolar electric mode is important and the optical interaction among indium clusters can be ignored. Therefore, we can conveniently adopt quasistatic approximation (QSA). Under QSA, the electromagnetic (EM) field scattered by indium clusters is identical to the field of a dipole $\boldsymbol{\mu}$ located at the center of this cluster.[5] The dipole is induced by the external field $\mathbf{E}$ and has the value of $\boldsymbol{\mu}=\alpha(\omega)\varepsilon_0\mathbf{E}$, where ε_0 is the vacuum permeability and the polarizability is

$$\alpha(\omega)=\frac{V}{\left(L+\frac{\varepsilon_{InN}}{\varepsilon_{In}-\varepsilon_{InN}}\right)}, \tag{1}$$

where V is the volume of indium cluster and L is the depolarization factor describing the shape of indium cluster.[6]

Since the interested spectral region is 0.7–6.5 eV, where InN show complex dielectric constants, the discussion of light scattering and absorption in InN should consider the absorbing medium. Here, we use the far-field approximation based on the asymptotic form of the EM field.[7] Under this approximation, Mundy *et al.*[8] defined the so-called unattenuated scattering and extinction. Combining the definitions of Mundy *et al.* with QSA, we will have the expressions for scattering cross section σ_{sca} and absorption cross section σ_{abs} as follows:

$$\sigma_{abs}=|k|\mathrm{Im}[\alpha(\omega)],$$

$$\sigma_{sca}=\frac{|k|^4}{6\pi}|\alpha(\omega)|^2, \tag{2}$$

with n_{InN} as the complex refraction index of InN, $k=2\pi/\lambda_{vac}n_{InN}$, λ_{vac} as the wavelength in vacuum, and Im[ ] as imaginary part. The dielectric constants of InN (indium) used throughout the paper were taken from Refs. 9 and 10.

Figures 1(a) and 1(b) display the spectral dependences of σ_{abs} and σ_{sca} for a 10 nm^3 sized indium cluster with different L value. In all ranges of photon energy, σ_{abs} is about 3–4 orders larger than σ_{sca}. So for small indium clusters, light extinction contributed by scattering can be ignored compared with absorption. The peaks in σ_{abs} and σ_{sca} are resulted from surface plasmon resonances (SPRs) or Mie resonances. For these peaks' positions ω_{SPR}, the condition $\mathrm{Re}[L+\varepsilon_{InN}(\omega)/\varepsilon_{In}(\omega)-\varepsilon_{InN}(\omega)]\approx 0$ is reached and the indium clusters dipole acquires a maximum value, greatly enhancing the capability of absorption and scattering. Also according to this condition, SPR peaks in σ_{sca} and σ_{abs} will both shift to lower energy if L is reduced. For indium spheres ($L_{indium}=1/3$), ω_{SPR} in absorption is around 3.4 eV. For $L_{indium}=0.07$, ω_{SPR} in absorption will shift to ~1 eV. This is the reason why Shubina *et al.* proposed that optical absorption of InN starting from 0.7 to 0.8 eV is not InN band edge absorption but indium related SPR. As seen in Fig. 1(c) (inset) in ordinary optical absorption configuration, with the electric polarization direction of incident light ($\vec{E}_{in}$) parallel to the sample surface, $L_{indium}=0.07$ indium cluster corresponds to the oblate interface indium inclusions.[3]

Because the bulk plasmon energy of indium 12 eV is far from proposed InN bandgap of 0.7–0.8 eV, in order to push the SPR into the range of 0.7–0.8 eV, one possible choice is to take a very small L value. However, it should be remembered that $\Sigma_{j=x,y,z}L_j=1$,[11] where L_j is the cluster's L value with $\vec{E}_{in}$ parallel to axis j (x,y,z are three axes vertical to each others). According to this requirement, the L value of the $L=0.07$ oblate interface indium inclusions of Shubina *et al.* will be 0.86 if $\vec{E}_{in}$ is changed to vertical to the sample

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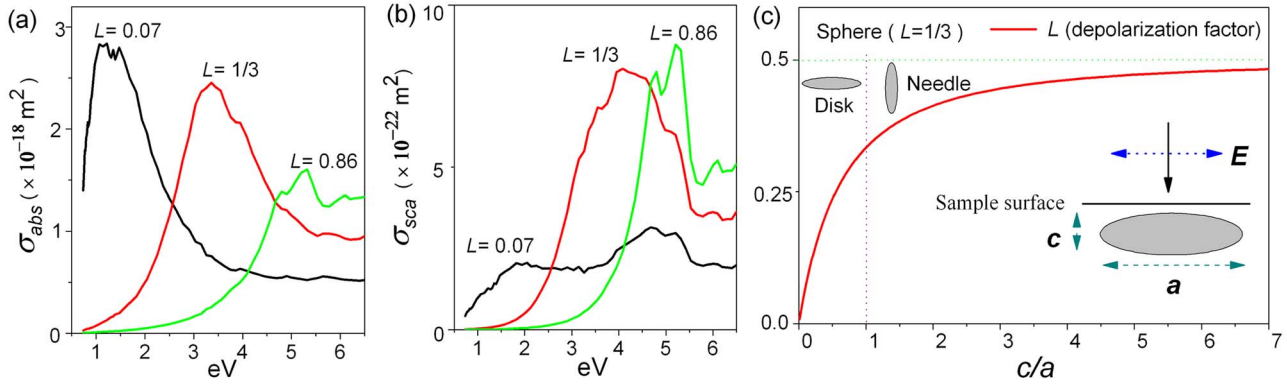

FIG. 1. (Color online) Spectral dependences of (a) σ_{abs} (absorption cross section) and (b) σ_{sca} (scattering cross section) for an indium cluster with different L value. The size of indium cluster is set to be 10 nm^3. Relationship between L and shape is in (c), Indium cluster is modeled by a spheroid, whose major axes are a and c and its shape will be remained if rotating around c. The inset in (c) shows the light absorption experiment configuration.

surface. It is not difficult to realize such configuration. For example, we can use TM light, whose $\vec{E}_{in}$ takes the same direction with light propagation direction, to irradiate the sample surface vertically. In this case, shown in Fig. 1(a), SPR light absorption peak from the indium clusters of Shubina *et al.* will shift to ultraviolet (~5.3 eV) and the "true" InN bandgap can be identified. Therefore, if InN bandgap is higher than ~0.7 eV, novel optical absorption anisotropy will be introduced with varying electric polarization direction of incident light. Unfortunately, such optical absorption anisotropy still lacks experimental supports and frustrates the meaningful viewpoints of Shubina *et al.*

On the other hand, due to the low melting temperature of indium, indium cluster will be in the form of liquid during growth. Because of the small size of indium clusters, its large surface tensions will prevail over its own weight and tend to form a solid sphere after cooling. Recent transmission electron microscopy observations of indium clusters in InN also show the indium cluster shape to be nearly sphere.[12,13] These two problems challenge the viewpoints of Shubina *et al.*

With a further increase of indium concentration C, mutual influence of metallic particles becomes important and QSA is invalidated. In order to address this issue, effective medium approximation (EMA),[14–17] which Maxwell–Garnett approximation can be resulted from, will be adopted below. In experiments, Losurdo *et al.* had reported their results on InN dielectric function containing indium,[9] as shown in Fig. 2(b) (inset), and we will use our theory to explain their results.

We want to admit the consideration of indium shape into EMA. Therefore, the self-consistency condition is rewritten as $\Sigma_i C_i(\varepsilon_i-\varepsilon_{eff})/\varepsilon_i+(1/L_i-1)\varepsilon_{eff}=0$,[14,15] where ε_i is the i component dielectric constants, L_i (C_i) is the depolarization factor (volume concentration) of i component. The optical properties of the composite are described by the effective dielectric constant ε_{eff}.

For InN:In composite, only two components are included, then we arrived at

$$C\frac{\varepsilon_{In}-\varepsilon_{eff}}{\varepsilon_{In}+\left(\frac{1}{L_{In}}-1\right)\varepsilon_{eff}}+(1-C)\frac{\varepsilon_{InN}-\varepsilon_{eff}}{\varepsilon_{InN}+\left(\frac{1}{L_{InN}}-1\right)\varepsilon_{eff}}=0, \tag{3}$$

where C is the metallic indium volume concentration. The solution to Eq. (3) is chosen with Im $\varepsilon_{eff}\geqslant 0$. Equation (3) can be generalized to many previous formalisms. When InN and In both are spheres ($L_{InN}=L_{In}=1/3$) or pillars with infinite length ($L_{InN}=L_{In}=\frac{1}{2}$), three-dimensional[15] or two-dimensional EMA is readily reached.[16,17]

Webman *et al.* had estimated through numerical calculations that EMA effective dielectric constant $\varepsilon_{eff}(\omega)$ of a binary inhomogeneous medium is valid for all possible C when the ratio $x(\omega)$ between the complex dielectric constants of the two components obeys the condition $0.05\leqslant|x(\omega)|\leqslant 20$.[15] The condition is fulfilled in the energy range of 0.8–6.5 eV considered here and slightly violated in 0.7–0.8 eV. In more infrared region, this condition will be seriously violated because of large negative value of ε_{In}. Violation of this condition make EMA inadequate in the vicinity of the percolation threshold $Cp=1/2$ (exactly in two dimensions) or $Cp=1/3$ (approximately in three dimensions) due to the percolation effect. The percolation occurring when C being near Cp is a critical phenomenon where physical properties of the composite have singularities and exhibit critical behaviors. Treatment of percolation is beyond the scope of EMA and this paper.

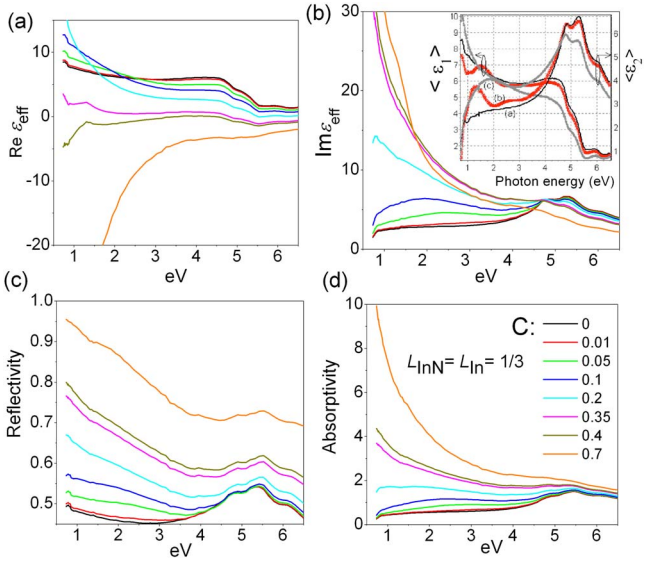

FIG. 2. (Color online) Spectral dependences of (a) real part and (b) imaginary part of ε_{eff} and (c) reflectivity and (d) absorptivity (imaginary part of refraction index). Inset in (b) the experimental results of M. Losurdo *et al.* [Fig. 4(a) in Ref. 9], with $\varepsilon_{sample}=\varepsilon_1+i\varepsilon_2$. Inset in (d): calculation parameters for Figs. 2(a)–2(d); indium clusters' shape is spheres.

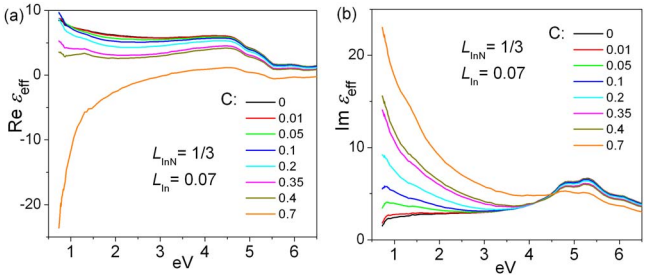

FIG. 3. (Color online) Spectral dependences of: (a) real part and (b) imaginary part of ε_{eff}. Different from Figs. 2(a) and 2(b) in indium clusters' disklike shape (L_{In}=0.07).

Figure 2 show the spectral dependences of real (Re ε_{eff}) and imaginary part of (Im ε_{eff}) of ε_{eff}, the reflection coefficient $r(r=|\sqrt{\varepsilon_{eff}}-1/\sqrt{\varepsilon_{eff}}+1|)$ and absorption coefficient (α =Im $\sqrt{\varepsilon_{eff}}$) of InN:In composite. We consider the general case $L_{InN}=L_{In}=\frac{1}{3}$ in Fig. 2. In near infrared region (~1 eV), when increasing C, Re ε_{eff} will first grow until C=20%. Then Re ε_{eff} will decrease, becoming negative when $C \geqslant 39\%$ and rushing down to Re ε_{indium}. However, in ultraviolet region (4–6.5 eV), increasing C will always reduce Re ε_{eff}. Visible region is a transition region between them. In respect to C, Im ε_{eff} shares similar behaviors with Re ε_{eff} but a different transition point ~4.7 eV when $C \leqslant 40\%$. For large C, the Im ε_{eff} will be close to Im ε_{indium}, reflecting the sample's transition to metallic indium. These characters above coincide well with Ref. 9.

We also notice the obvious structures in Re ε_{eff} and weak ones in Im ε_{eff} around 1.5 eV when C becomes large [C=0.35 in Fig. 2(a)]. The structures were also observed by Losurdo *et al.* [inset of Fig. 2(b), curve (b)]. Since these structures do not shift by varying indium cluster shape (Fig. 3) and concentration, they should not be attributed to SPR. It is known that, indium, not being an ideal metal, has a strong interband absorption peaking at 1.4 eV,[10,18] which add a wave-packet increase in Im(ε_{In}) and an oscillation in Re (ε_{In}) both centered at 1.4 eV to the background of Drude metal dielectric constants. On the other hand, when photon energy increases beyond InN band edge ~0.7 eV, there are a relatively fast decreased Re (ε_{InN}) and an also fast increased Im(ε_{InN}). These mixed contributions from InN and indium will come together to produce the structure ranging from 0.7 to 3 eV. When C is near the percolation threshold Cp, ε_{eff} shows the maximum sensitivity to the material parameter of the composite, such as C, ε_{InN}, and ε_{In}, leading to the clearest observation of such complex structures. Although Losurdo *et al.* thought those structures may interfere in determination of InN bandgap, we have shown their appearances need detectable indium concentration (in the order of 10%) and are easy to be removed through using InN sample with little or even medium phase separation.

In an overall view, our results above can explain the experimental observations in Ref. 9. It is noted that even the C=0.1 curve in Figs. 2(a) and 2(b) agree well with curve (c) in Ref. 9 both qualitatively and quantitatively. We can also explain the structures in 1–3 eV for curve (b) in Ref. 9 but not well in quantity. Losurdo *et al.* did not give their samples' metallic indium concentration, but judging from the atomic force microscopy image, we think curve (b) is the sample with higher C value than curve (c). So we conclude that the appearances of structures in 1–3 eV need large C value near Cp, which makes EMA a bad approximation in quantity. We predict that such structures will be indistinct if C increases further beyond Cp.

As shown in Figs. 2(c) and 2(d), compared with ε_{eff}, the rules governing reflection, absorption is rather simple, a increase of C will always enhance the composite reflection, absorption capability. Due to the large value of Im ε_{InN} and Im ε_{In}, SPR effect is of little strength and difficult to manifest itself. The influence of indium shape on ε_{eff} is presented in Fig. 3, the results are not so different from the situation of spheres in Figs. 2(a) and 2(b) except some quantitative details. For low C value, SPR peak around 1 eV produced by low density L_{In}=0.07 indium clusters is covering up by strong InN interband absorption above 0.7 eV. When C is large and interclusters optical interaction will tend to smear out the cluster individual characters, the importance of cluster shape is reduced, only resulting in some quantitative changes.

In summary, we have systematically analyzed the impact of metallic indium clusters on the optical properties of InN. The InN:In composite dielectric function calculated by our EMA results are in satisfactory agreement with experimental results. It demonstrates that QSA and EMA can be adopted for describing InN with phase separation.

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan through Grant-in-Aid for Scientific Research in Priority Areas (No. 18069005).

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