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Novel semiconducting materials for optoelectronic applications: $Al_{1-x}Tl_xN$ alloys

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We proprose the ternary semiconducting $Al_{1-x}Tl_xN$ alloys as new material for optoelectronic applications. *Ab initio* calculations have been performed to study structural, electronic, and optical properties of the theoretically designed thallium-aluminum based nitride alloys. We found that the lattice constants vary linearly with thallium composition whereas the band gap and absorption edge span from ultraviolet to infrared energy region by increasing thallium content which make the predicted material interesting for infrared optical devices among other technological applications. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2901146]

The nitride semiconductors such as AlN, GaN, and InN have good thermal and chemical stabilities that are important in technological applications. These compounds are currently being studied because of their great potential for telecommunications electronics, light emitting diodes, and lasers.[1] They can be used for emission of light in green, blue, and ultraviolet regions of the light spectrum that were not previously accessible with solid state light emitters.[2]

On the other hand, there have been a great interest to study III-V semiconductors containing thallium aiming to narrow the band gap down to the infrared energy region.[3–7] For example, Yamamoto *et al.*[5] were able to grow the ternary alloys $Tl_xIn_{1-x}P$ on top of (100) InP substrate while Beneyton *et al.*[6] synthesized $Tl_xGa_{1-x}As$ and $Tl_xIn_{1-x}As$ alloys by molecular-beam epitaxy. Additionally, Kajikawa *et al.*[7] reported the growth of $Tl_xGa_{1-x}As$ alloys also by molecular-beam epitaxy.

In this paper, we propose $Al_{1-x}Tl_xN$ alloys as new material for optoelectronic devices. We investigate the structural, electronic, and optical properties of $Al_{1-x}Tl_xN$ alloys by using first principles calculations based on density functional theory.[8] The great advantage of alloying materials is the possibility of control their physical properties. For instance, AlN is a wide band gap semiconductor while the band gap of TlN is nearly 0 eV. By alloying AlN and TlN, the energy band gap can, in principle, vary from near infrared to ultraviolet energy region which could certainly lead to new properties with great potential for infrared optical devices.

The geometry optimization of the crystal structures of $Al_{1-x}Tl_xN$ alloys was calculated using the projected augmented wave method as implemented in VASP code.[9] The crystal structure for each alloy composition was optimized at its volume by force and stress minimization until the Hellman–Feynman forces become smaller than 10^{-3} eV/Å and the total energies converged to below 10^{-4} eV, with respect to the Brillouin zone integration. To calculate the electronic and optical properties of $Al_{1-x}Tl_xN$ alloys, we used the full-potential linearized augmented plane wave method as implemented in Wien2k code.[10] In all set of calculations, the exchange and correlation potential in the generalized gradient approximation (GGA) within the Perdew–Wang parametrization was used[11] and a mesh of about 65 k points generated according to the Monkhorst–Pack scheme[12] was sufficient to achieve the convergence.

The III-nitride compounds can be grown either in zinc blende or wurtzite crystal structure depending on the experimental conditions. For instance, Li *et al.*[13] obtained AlN samples in zinc-blende structure by using ball milling experiments while Vogg *et al.*[14] found wurtzite AlN by growing it on top of diamond substrates. To date, the synthesis of TlN samples has not yet been reported. However, Zaoui[15] and Ferhat and Zaoui[16] put forward its ground-state structure by *ab initio* calculations. Initially, they found that wurtzite structure is more stable phase than zinc blende and PbO phases for TlN. Later on, Houat *et al.*[17] extended the work by considering other crystal phases for TlN such as CsCl, Cmcm, and rock salt. The conclusions remained unchanged and it was found that the wurtzite phase is the most stable one but it is nearly degenerated with zinc-blende phase. The electronic and optical properties of zinc-blende and wurtzite phases of TlN have been reported by Ferreira da Silva *et al.*[18]

To model $Al_{1-x}Tl_xN$ alloys we can use both zinc-blende or wurtzite crystal structures. In the present study, we have investigated the physical properties of the alloys using zinc-blende-like crystal structures while the modeling of wurtzite-like structures will be published elsewhere.[19] Ordering of alloys can sometimes be very important for some alloys such as GaAsN.[20,21] In this work, we show the results for highly ordered system obtained using an 8 atom supercell. The aluminum atoms in the cell were replaced by thallium atoms

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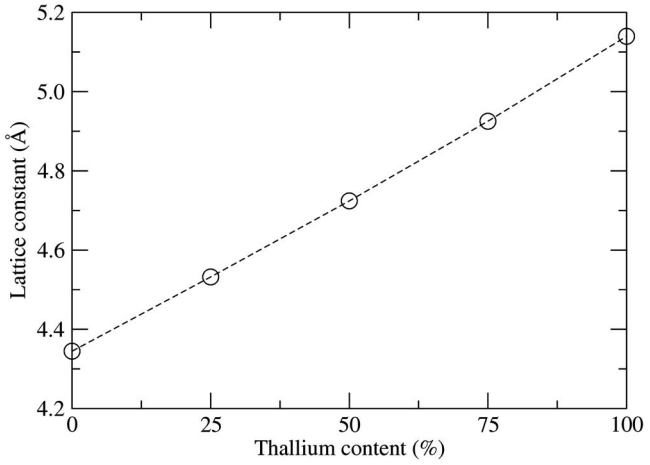

FIG. 1. Lattice constant of $Al_{1-x}Tl_xN$ as a function of thallium content.

in such way that leads to the desired alloy compositions. This procedure to model alloys with satisfactory results has also been applied for other alloys such as $Si_{1-x}Ge_x$ and $Be_xZn_{1-x}Te$.[22,23]

In Fig. 1, we show the lattice constants of $Al_{1-x}Tl_xN$ alloys as a function of thallium content. Similarly to other nitride alloys such as $Al_{1-x}Ga_xN$,[24] we found that the lattice constants of $Al_{1-x}Tl_xN$ alloys vary linearly with the alloy composition following the so-called Vegard's rule. The lattice constants obey the equation

$$a = 4.3368 + 0.0079x \text{ (Å)}, \tag{1}$$

which is in good agreement with the previously reported values for the binary cases, AlN[1,25] and TlN.[15,16,18] From Fig. 1, we see that the lattice mismatch between $x=0$ and $x=25\%$ of thallium content is less than 5% which make potentially possible the growing of $Al_{0.75}Tl_{0.25}N$ on top of AlN substrates.

The electronic properties of $Al_{1-x}Tl_xN$ alloys have been studied by the density of states (DOS). In Fig. 2, we plot the DOS of $Al_{1-x}Tl_xN$ alloys for four different thallium compositions, namely, 0%, 25%, 50%, and 75%. From Figs. 2(a)–2(d), we see that both valence and conduction bands are

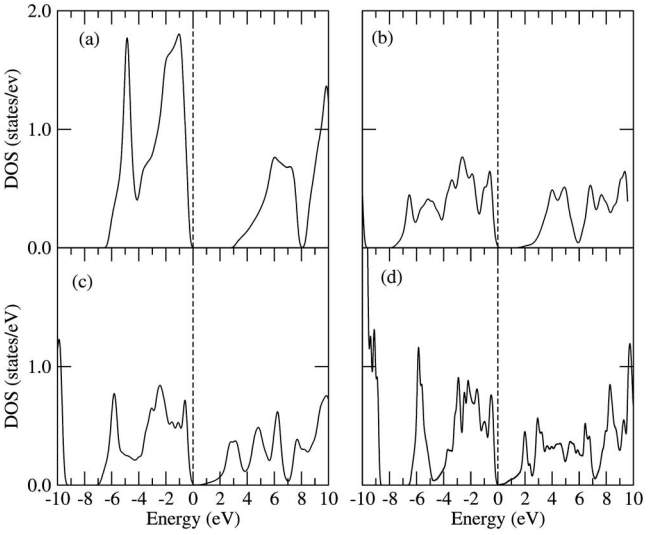

FIG. 2. Density of states of $Al_{1-x}Tl_xN$ alloys for $x=0.00$ (a), 0.25 (b), 0.50 (c), and 0.75 (d) of thallium content. The valence-band maximum is indicated by a vertical dashed line.

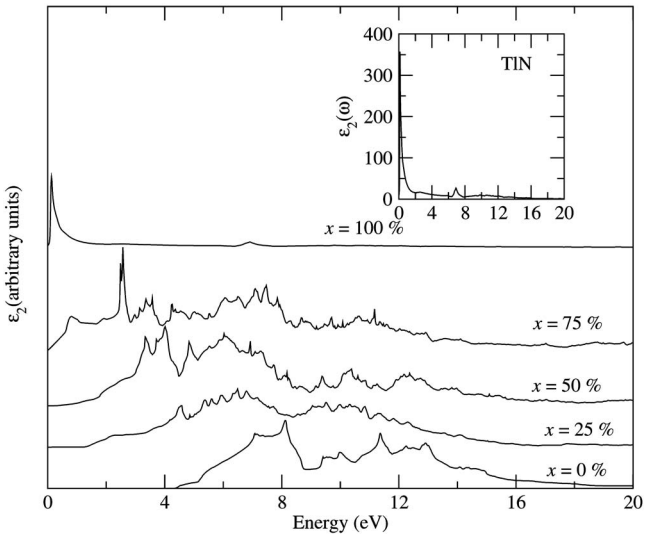

FIG. 3. Imaginary part of the dielectric function $Al_{1-x}Tl_xN$ alloys vs photon energy for several different thallium compositions. The inset show the very high absorption at low energy region for TlN.

wider by increasing the amount of thallium. The two lower subbands which form the conduction bands in Fig. 2(a) are merged forming a single conduction band having more features when the amount of thallium is increased as can be seen in Figs. 2(b)–2(d). For AlN ($x=0$), the theoretical indirect GGA band gap is nearly 3 eV and it is reduced by increasing the amount of thallium in the alloys. In the other composition extreme (TlN), the band gap becomes zero. Here, we have also performed calculations including spin-orbit interactions and we find a band gap of about 50 meV for TlN. Similarly, the band gap of $Al_{1-x}Tl_xN$ alloys is reduced by increasing the thallium content as its narrowing in group III-nitride when increasing the atomic number of the chemical element of group III of the periodic table. Alloys with different sizes of the substitutional atoms may experience strong band-gap bowing with respect to composition. Knowing this bowing is crucial for understanding the alloy properties; a recent study[26] explores that a strong band bowing can be utilized to modify the dopability of the material. Fitting the gap energy to a parabolic expression, defining the bowing coefficient $b(E_g)$, we find the band gap to be $E_g(x)=E_g(\text{AlN})(1-x)+E_g(\text{TlN})x-b(E_g)(1-x)x$ with $b(E_g)=5.29$ eV. For $x \geqslant 0.5$, the gap is close to zero and thus the most important composition region for alloying is $x<0.5$.

We study the optical properties of the $Al_{1-x}Tl_xN$ alloys by calculating the imaginary part of the dielectric function which can be directly obtained from the electronic structure using the joint DOS and the matrix elements of the momentum **p** between occupied and unoccupied eigenstates

$$\epsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{\mathbf{k}nn'} \langle \mathbf{k}n|p_i|\mathbf{k}n'\rangle\langle \mathbf{k}n'|p_j|\mathbf{k}n\rangle \times f_{\mathbf{k}n}(1-f_{\mathbf{k}n'})\delta(E_{\mathbf{k}n'}-E_{\mathbf{k}n}-\hbar\omega). \tag{2}$$

In this equation, e is the electron charge, m is its mass, Ω is the volume of crystal, $f_{\mathbf{k}n}$ is the Fermi distribution function and $|\mathbf{k}n\rangle$ is the crystal wave function corresponding to the n^{th} eigenvalue $E_{\mathbf{k}n}$ with crystal wave vector **k**.

The optical properties of AlN and TlN have been discussed in details before and we refer the reader to the Refs. 18 and 27.

In Fig. 3, we show the optical properties of $Al_{1-x}Tl_xN$ alloys for thallium compositions from $x=0$ until $x=100\%$. We find that the absorption edge is moving downward in energy when the thallium content in the alloy is increased. Indeed, the absorption edge changes from almost 4 eV when considering the AlN case to almost 50 meV in the case of TlN. We should also point out that TlN is found to have a nearly metallic behavior having a very high absorption in the low energy range as can be seen in the inset of Fig. 3. Therefore, with very small change in the Tl composition, the materials can thus change from semiconductor to metal and that can be benefited in device structures.

To conclude, we have used first-principles calculations to investigate the physical properties of $Al_{1-x}Tl_xN$ alloys. We show that the lattice constants of the $Al_{1-x}Tl_xN$ alloys follow a linear equation by varying the thallium composition such as other III-nitride alloys. The band gap and absorption edge of the alloys span from ultraviolet to infrared energy regions by increase the alloy composition. Additionally, we found that the spin-orbit effects open up a small gap in TlN resulting in a nearly metallic behavior of its optical response. We also found that with a small incorporation of Tl, the alloys can thus change from semiconductor to metal and that can be useful in device structures. We therefore propose $Al_{1-x}Tl_xN$ alloys as new material to be used in infrared optical devices to benefit from its very strong band gap dependence with respect to alloy composition.

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