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Negative electron affinity material: LaS on InP

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Rare-earth monosulfides are shown to offer attractive alternatives to the commonly used cesiated surfaces to reach negative electron affinity at various III-V semiconductor surfaces. This is illustrated by theoretical calculations of metallic overlayers of LaS on a semiconducting InP substrate using first-principles techniques. The combination of these materials is demonstrated to result in a very low work function (0.8 eV). The interface between the LaS overlayer/InP substrate is shown to be quite stable, and the lattice relaxation of the surface atoms and the atoms at the interface is found to be small.

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Over the last 30 years, a large number of cold cathode and photocathode structures with semiconductor materials have been proposed.[1,2] Negative electron affinity (NEA) in such structures is achieved by interfacing a wide band gap semiconductor with a low work-function (WF) material such that the surface vacuum barrier is brought below the bulk conduction band edge.[3] The practical implications of low work-function cold cathode emitter materials lies primarily in their applications in microwave vacuum transistors and tubes, pressure sensors, thin panel displays, high temperature and radiation tolerant sensors. However, the search for materials combinations with optimized efficiency in these devices calls for a thorough microscopical understanding of these materials. In the past it has been demonstrated that there are numerous unanswered questions or unresolved issues on the materials properties of these systems and a complete optimization of low work-function materials has not yet been made. It is the purpose of this paper to point towards a different class of materials and we suggest here, using first-principles theoretical calculations, a thin film material that has vastly improved properties for use as a cold electron-emitter material.

For an electron emitter to be useful in practical applications it should be chemically stable and provide uniform current densities for operational lifetimes over 10^5 h. Alkali metal (Cs) films on emitter surfaces are widely used.[3] However, cesiated semiconductor surfaces have several limitations including poor chemical stability of the cesium atoms, a low melting point $(28.5\,^\circ\mathrm{C})$, and high vapor pressure of Cs $(10^{-3}$ torr at $100\,^\circ\mathrm{C})$. Furthermore, accelerated cathode degradation occurs under high current operating conditions due to electron stimulated desorption of the Cs activation layer.[4]

Recently, a more stable approach to reach NEA at semiconductor surfaces based on the use of chalcogenides of the rare-earth elements was suggested.[5,6] Rare-earth monosulfides are unusual in many respects. Not only do they possess high chemical stability (melting temperatures above $2000\,^\circ\mathrm{C})$, but they also display metallic conduction. Material properties of selected cubic rare-earth sulfides are summarized in Table I. Of particular interest is the fact that in bulk phase, the room-temperature WF of the rare-earth chalcogenides, when extrapolated from high-temperature measurements,[7] is quite small, suggesting that when deposited on *p*-type doped semiconductors these materials might be used to reach NEA. In addition the lattice matching is good, LaS has a lattice constant (5.854 Å) very close to that of InP (5.869 Å), while for instance NdS has a lattice constant (5.69 Å) very close to that of GaAs (5.653 Å). Since the extrapolated room-temperature WF of LaS (1.14 eV) and NdS (1.36 eV) are below the band gap of InP (1.35 eV) and GaAs (1.41 eV), respectively, NEA could, therefore, be realized at InP/LaS (and GaAs/NdS) interfaces using heavily *p*-type doped semiconductors. However, it is far from clear that the work-function of rare-earth chalcogenides, when grown as thin films on top of InP (or GaAs), is sufficiently low to enable NEA, nor is it known if, on energetic grounds, the growth of these films can be achieved. The proposed ideas must hence be confirmed by experimental work or quantitative theoretical calculations.

It is the purpose of this paper to demonstrate that NEA can indeed be achieved for thin layers of LaS on an InP substrate, by calculating the electronic structure, work-function, and adhesive properties of this system, using a first-principles technique. The calculational method used in the present work is a so-called full-potential linear muffin-tin orbital (LMTO) method, for bulk[8] and slab geometries,[9] which is based on the local-density approximation (LSDA) (Ref. 10) or generalized gradient approximation (GGA) (Ref. 11) to density functional theory. In the bulk calculations we adopt a base geometry consisting of muffin-tin spheres and an interstitial region, whereas for the slab calculations we

TABLE I. Materials parameters of rare-earth sulfides (cubic form): *a* (lattice constant in Å), WF (extrapolated work function at room temperature, in eV), T_m (melting point in °C), and ρ electrical resistivity (in $\mu\Omega$ cm) (Ref. 7).

	ErS	YS	NdS	GdS	PrS	CeS	LaS	EuS	SmS
a	5.424	5.466	5.69	5.74	5.747	5.778	5.854	5.968	5.970
WF			1.36		1.26	1.05	1.14		
T_m		2060	2200		2230	2450	2200		1870
ρ			242		240	170	25		

also introduce a vacuum region.[9] The interstitial basis function is a Bloch sum of Neuman and Hankel functions. Each Neuman or Hankel function is then augmented (replaced) by a numerical basis function inside the muffin-tin spheres, in the standard way of the linear muffin-tin orbital method.[12] In the slab method the Neuman and Hankel functions are replaced by numerical functions also in the vacuum region.

The present calculations are all-electron as well as scalar relativistic. The latter is achieved by including the mass velocity and Darwin terms (and higher-order terms) in the calculation of the radial functions, inside the muffin-tin spheres, whereas the spin-orbit coupling was omitted. Moreover, the present calculations made use of a so-called double basis, to ensure a well converged basis set. This means that we used two Hankel or Neuman functions each attaching to its own radial function for each set of (n,l)-quantum number. We thus had a set of two $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ basis functions centered on the La atom and two $3s$, $3p$, and $3d$ basis functions centered on the S and P atoms. Moreover, we used two $5s$, $5p$, and $4d$ basis functions on the In atom. The calculations were made with 9 InP layers sandwiched between 3 LaS layers on each side. In this way both the interface electronic structure and geometry is obtained in parallel to information about the surface electronic structure and geometry of the InP/LaS system. The geometry of the presently studied LaS overlayer on InP is shown in Fig. 1.

We initiated our computational study by calculating the lattice constant of InP. The total energy was minimized for a constant of 11.11 a.u (5.879 Å) that should be compared to the experimental value of 11.09 a.u (5.869 Å). This calculation was mainly done as a reference to investigate the accuracy of our computational scheme for these systems. In our previous work[13] we found that the theoretical lattice constant of bulk LaS is 10.91 a.u (5.773 Å) that agrees well with the experimental value of 11.06 a.u (5.854 Å). For the calculation of the LaS overlayer on the InP compound we kept the in-plane lattice constant fixed and equal to the theoretical lattice constant of InP. Next, we performed a geometry optimization of the atomic positions of the LaS/InP interface, which resulted in a distance between the La atoms in the LaS-overlayer and the P atoms in the InP substrate that is very close to the interatomic distances between the In and P atoms of the substrate. The geometry optimization of the surface layer resulted in a small but non-negligible contraction of 0.2% from the positions given by the ideal NaCl structure. This is in rather good agreement with our previous study of LaS on CdS,[13] where the surface layer of LaS relaxed inward with 0.5%. This demonstrates that if one were to realize a growth of LaS on InP it would produce atomic distances that do not deviate from the interatomic distances in bulk InP and LaS.

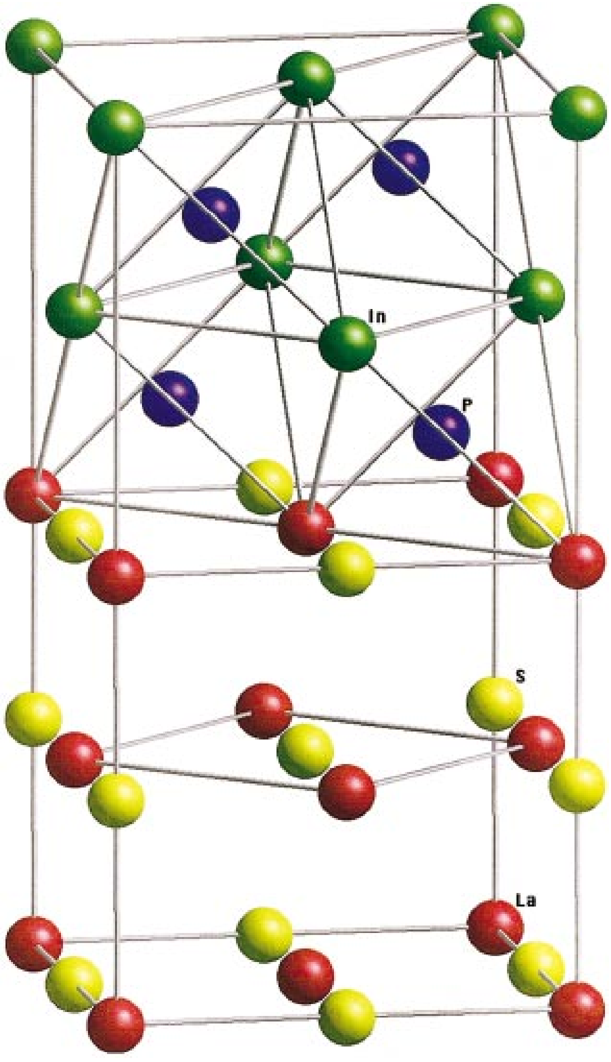

FIG. 1. (Color) Figure of the geometry of the unit cell used in the calculations. Green atoms represent In, blue P, yellow S, and red La atoms.

From the calculated optimized atomic geometry we then calculated the charge density and the density of states (DOS). The charge density is shown in Fig. 2. One may observe from these figures that the density of the LaS overlayer is representative of metallic bonding, with an absence of directionality of the density between the atoms. For the atoms in the InP substrate the situation is different since the charge piling up between the atoms is obvious and the chemical bonding has a strong covalent character. The charge density in the region in between the substrate and the overlayer shows little effects of directionality and the transition from covalent bonds in the substrate to metallic in the overlayer is seen to be abrupt.

In Fig. 3 we show the DOS projected on different atomic layers, the LaS surface, the LaS interface, the InP interface, and on the InP layers below the InP interface. In Fig. 3, we first observe that both InP layers shown in the figure are actually metallic since they have a finite, albeit small, DOS at the Fermi level (E_F). Next, we observe that the $4f$ bands form a narrow resonance a few tenths of a Rydberg above E_F, and that there is a chemical shift between the position of the $4f$ bands at the surface and interface. Our calculations show that the $4f$ bands of the surface atoms are closer to E_F compared to the La atom at the interface with the substrate. The position of these narrow bands has previously been discussed to possibly be crucial for enabling the cold electron emission.[13] In addition we note that the position of the Fermi level is such that it lies just above the valence band of the InP

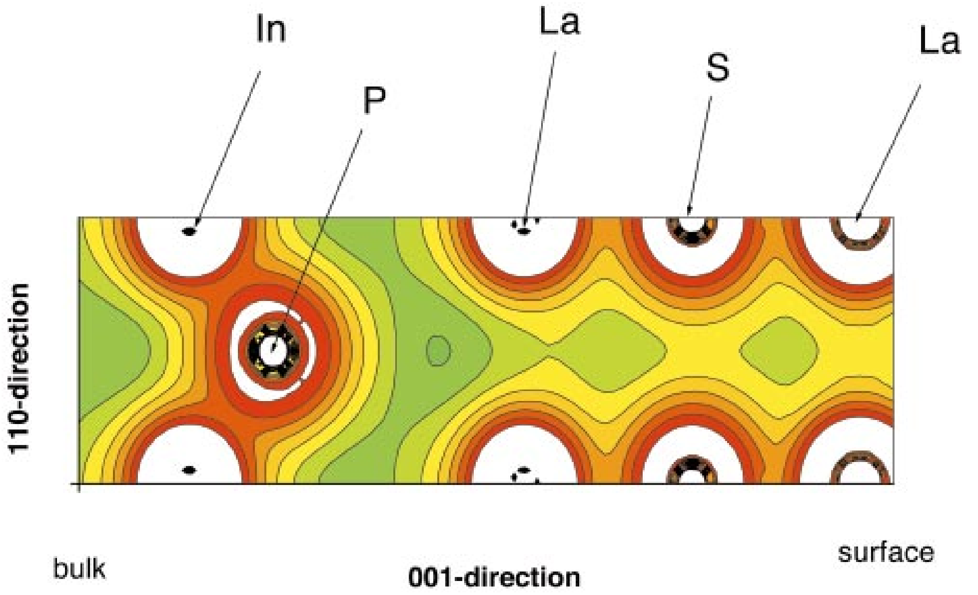

FIG. 2. (Color) Charge density contour of InP/LaS. The cut is for a 110 plane.

substrate, suggesting that the deposition of a few monolayers of LaS on heavily-doped *p*-type InP substrate would provide a quite stable NEA cathode or NEA photocathode.[3]

The calculated work-function of the LaS/InP system, the most central result of our study, is exceptionally low, 0.8 eV. Based on this result we conclude that the LaS/InP system is very promising as a NEA material, especially if a thin film that resembles our presently studied geometry is grown. In addition our calculations demonstrate that the growth of LaS on InP should, on energetic grounds, be stable, since the total energy of our LaS/InP system is lower than LaS separated from the InP substrate. Hence, theory shows both that the growth of these materials should be possible and that the workfunction is lower than the bandgap of the InP substrate, enabling the use of this material as cold electron emitters.

To summarize our findings we propose that thin films of LaS (a few atomic layers thick to avoid the effects of inelastic scattering in LaS) on an InP substrate should grow in a well controlled epitaxial way, without large lattice distortions of InP or LaS, using, for instance, rf magnetron sputtering. The calculated electronic structure reveals a smooth transition from metallic to semiconducting behavior that takes place over several atomic layers, whereas the nature of the chemical bonding changes more abruptly at the LaS/InP interface. The work-function of these films is found to be exceptionally low, enabling the use of a heavily doped *p*-type

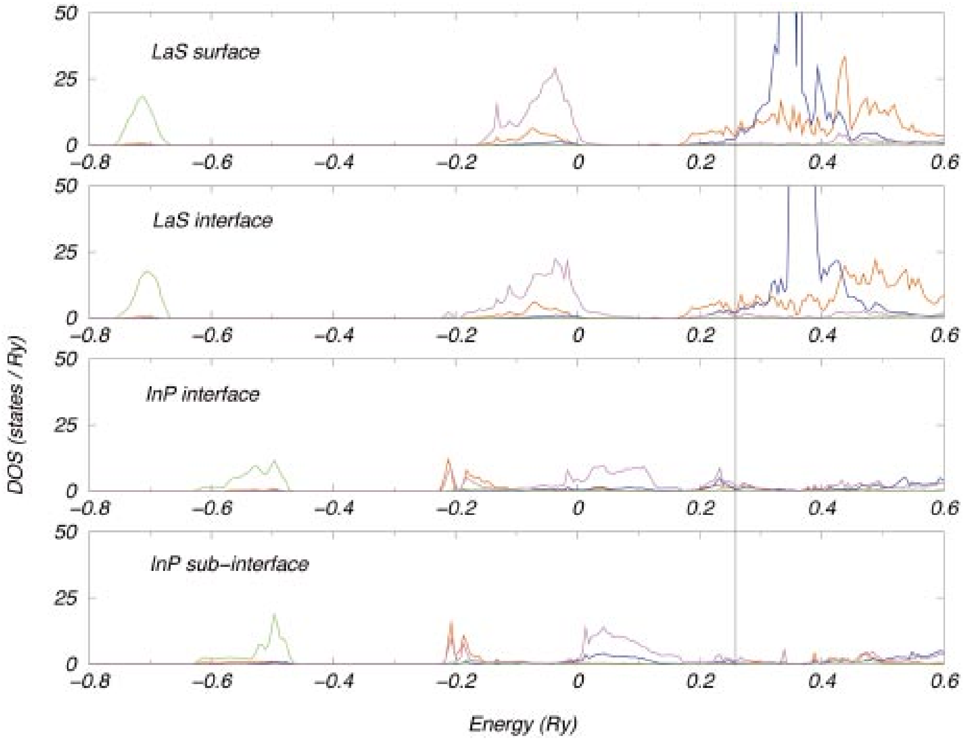

FIG. 3. (Color) Calculated density of states (DOS) for a slab of InP/LaS. The top panel shows the DOS projected on the surface layer and the second panel the DOS projected on the LaS atoms at the interface. In these two panels the La $5d$ states are shown in red, the La $4f$ states in blue, the S $3s$ states are shown as green, and the S $3p$ states are plotted in magenta. In the third panel the DOS is projected on the InP interface atoms and the lowest panel shows the DOS projected on the atomic layer of InP just below the interface. In these two panels In $5s$ states are shown as red, In $5p$ states as blue, P 3s states as green, and P $3p$ states as magenta. Energy is in Rydbergs and the Fermi level is marked by a vertical line.

InP substrate with LaS films on top as highly stable cold cathodes with high enough emission current densities (mA/cm^2) for flat panel display applications. Higher emission current densities (1–100 A/cm^2), more suitable for microwave transistors and tubes, could eventually be reached with other cold cathode configurations, such as *n*-InP/*p*-InP/LaS or *n*-InP/*p*-InAlAs/LaS. For other III-V materials, a fine tuning of the electronic and atomic structure will require alloying with other rare-earth elements and the exploration of other substrate configurations. This is outside the scope of the present presentation and will be communicated elsewhere.[14]

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