Inherent Enhancement of Electronic Emission from Hexaboride Heterostructure

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Based on a nonequilibrium Green's-function approach to the calculation of emission currents from first principles, we show that cathodes consisting of LaB_6/BaB_6 superlattices can yield an order-of-magnitude higher thermionic current densities than pure LaB_6 cathodes. Because of a 0.46-eV lowering of the work function, such a heterostructure cathode could thus be operated at significantly lower temperatures. Neither the stability nor the magnitude of electronic tunneling coefficients is compromised in the superlattice system as compared to pure LaB_6, which is in contrast to the generally reduced stability and large dipole barriers in the case of adsorbate-induced lowering of the work function. The heterostructure could thus be used as a cathode material that at the same time is stable and has emission properties superior to those of pure LaB_6.

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I. INTRODUCTION

Lanthanum hexaboride LaB_6 is one of the most-often-used cathode materials in thermionic emitters [1,2], and it has also been demonstrated to provide a bright source for field emission in the form of emitter arrays [3] and nanowires [4–7]. The advantages of LaB_6 as a cathode material lie in the fact that it exhibits both thermal stability and a low work function of its most stable surface orientation [100] [8,9]. This behavior is in contrast to, e.g., the trends in the periodic table, where low work function always means a relatively low melting point. In addition, the evaporation rate of surface atoms is low even at elevated temperatures and similar for La and B atoms [10–12], such that the [100] surface remains terminated with La atoms over time [13].

The emission properties of LaB_6 could be improved by lowering its work function, either through adsorbates or through modification of the bulk structure. Adsorption of alkali or alkali-earth atoms can reduce the work function of metal surfaces significantly through the formation of strong surface dipoles. This mechanism is particularly effective if the bare-metal surface has a high work function, leading to a large dipole due to transfer of the loosely bound outer *s* electrons of the adsorbates. If the work function of the bare metal is low—which is the case for $LaB_6(100)$—the binding of the adsorbates will be relatively weak and the induced surface dipoles will be small. Adsorbing, e.g., a monolayer of O on $LaB_6(100)$ first and then adsorbing Cs increases the desorption temperature of Cs to about 1000 K, but the observed work function is more than 1 eV higher than that of bare $LaB_6(100)$, since the O layer causes an increase in the work function [14].

Alloying of LaB_6 with other hexaborides has also been considered to improve emission [15–22]. First studies of such mixed hexaborides, where the crystals were grown from aluminum flux [16,23], did not yield an increase in thermionic current densities [15]. According to density-functional-theory (DFT) calculations, replacing La with Ba in the surface layer should decrease the work function [24], however, such a surface layer would evaporate within seconds at elevated temperatures [12]. Later experiments demonstrated bulk substitution of Ba for La in LaB_6 using a spark-plasma sintering process with an increase of the lattice constants of the hexaboride [25], and Liu *et al.* [18] showed enhanced thermionic emission of LaB_6 and BaB_6 mixtures (for the latter experiments, no crystal structure analysis was provided).

Here, we show based on DFT calculations that epitaxial LaB_6/BaB_6 superstructures are more stable than their phase-separated constituents and that the work function of such a structure is 0.46 eV lower than that of pure LaB_6. Using first-principles transport calculations, we find that the tunneling probabilities are of the same magnitude as those for pure LaB_6 despite the lowered work function. This LaB_6/BaB_6 heterostructure would thus provide a cathode material combining good stability with emission properties superior to those of pure LaB_6.

II. DETAILS OF CALCULATION

DFT calculations are performed with the DACAPO [26] ultrasoft pseudopotential [27] code, using the Perdew-Burke-Ernzerhof [28] exchange-correlation functional.

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Kohn-Sham states are expanded in plane-wave basis sets with a cutoff of 400 eV (benchmark calculations using hard projector-augmented wave potentials [29] as implemented in the QUANTUM ESPRESSO [30] code at a plane-wave cutoff of 2000 eV differ by less than 50 meV from the work functions obtained with the softer ultrasoft pseudopotentials used here). For the optimization of lattice constants, an increased cutoff of 800 eV is used to reduce spurious Pulay stress [31]. Brillouin zones are sampled with k-point spacings of at most ~ 0.1 Å^{-1}. Fermi surface smearing is performed using Fermi-Dirac statistics with temperatures $k_B T \geq 0.1$ eV (k_B denotes Boltzmann's constant) to determine the temperature dependence of the Fermi level. Transformation of Bloch states to Wannier functions used in the transport calculations is performed with the ASE software package [32,33].

The transport calculations are based on a recently developed [34] nonequilibrium Green's-function approach [35,36], where bulk metallic lead and vacuum are treated as semi-infinite systems. Bulk metal and vacuum are the source and drain for electrons, respectively. Using the Landauer-Büttiker formalism [37,38], we calculate the thermionic current density as

$$J(T) = \frac{1}{\pi S} \int dE f[E - \mu(T), T] \mathcal{T}(E), \qquad (1)$$

where the metallic lead and vacuum are held at temperatures T and 0 K, respectively. The temperature dependence of the work function of the slab is taken into account here only through the temperature dependence of the Fermi level $\mu(T)$. $f[E - \mu(T), T]$ is the Fermi-Dirac distribution. $\mathcal{T}(E)$ is the transmission function of the considered surface with surface area S. The calculation of $\mathcal{T}(E)$ is based on DFT Hamiltonians in Wannier-function basis sets for metallic lead and slab, while the vacuum states are represented as plane waves (see Ref. [34] for details). We neglect thermal expansion of the lattice, which is a good approximation due to a low expansion coefficient of LaB_6 of 6×10^{-6} K^{-1} [39].

For LaB_6 and LaB_6/BaB_6, the considered slabs consist of four and five layers of hexaboride with an additional terminating layer of La and Ba, respectively. The two topmost hexaboride layers are allowed to relax, and a dipole correction [40] is applied.

III. RESULTS

A. Thermodynamic properties

We consider heterostructures with alternating single layers of LaB_6 and BaB_6, i.e., with chemical formula $LaBaB_{12}$. Based on DFT total-energy calculations of bulk structures with alternating layers, we find that the [100] growth direction would be energetically preferred over the [110] and [111] directions by 65 and 24 meV per formula unit $LaBaB_{12}$, respectively. We will thus focus on the heterostructure with [100] as layer normal, and it will hence be straightforward to directly compare structural properties such as relaxation of the (100) surfaces of LaB_6 and LaB_6/BaB_6.

The bulk structure of LaB_6/BaB_6 with growth direction [100] is 0.18 eV more stable per formula unit $LaBaB_{12}$ than phase-separated LaB_6 and BaB_6. The DFT-optimized lattice constants are 8.39 Å for the [100] and 4.19 Å for the perpendicular directions. The optimized lattice constants of LaB_6 and BaB_6 are 4.15 and 4.24 Å, respectively. The lattice spacing in the heterostructure is approximately the arithmetic mean of the spacing in the constituent hexaboride phases.

To calculate the preferred termination of the $LaB_6/BaB_6(100)$ surface, we consider a slab terminated by Ba atoms on one face and by La atoms on the other. Referencing to the cohesive energies of bulk Ba and La, removal of the BaB_6 surface layer is 0.4 eV more expensive per hexaboride unit than removing the LaB_6 surface layer on the other face. Termination of the heterostructure with Ba atoms is thus thermodynamically preferred (termination with B atoms is several eV more expensive per removed Ba atom). The corresponding Ba-terminated surface is depicted in Fig. 1. When surface layers begin to evaporate at elevated temperatures, there will be a strong thermodynamic driving force for diffusion of Ba atoms to the surface: the energy of the La-terminated system is lowered by 0.28 eV for exchange of a surface La atom with a subsurface Ba atom. Therefore, the $LaB_6/BaB_6(100)$ surface should be replenished with terminating Ba atoms during thermionic operation.

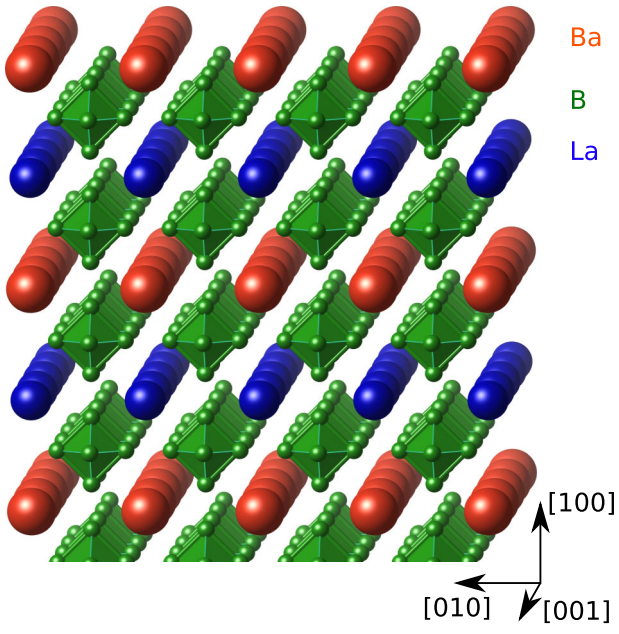

FIG. 1. Scheme [41] of the Ba-terminated LaB_6/BaB_6 surface with growth direction [100]. La is depicted by blue spheres, Ba by orange spheres, and B_6 octahedra are represented in green color.

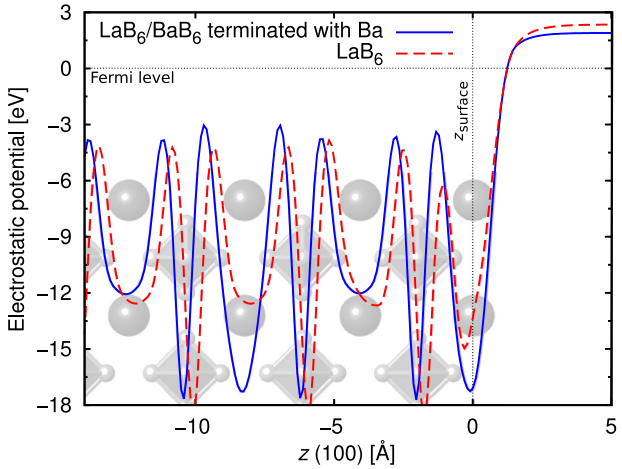

FIG. 2. Average electrostatic potential along the [100] direction of Ba-terminated $LaB_6/BaB_6(100)$ and $LaB_6(100)$. The horizontal and vertical dotted lines represent the Fermi level and the position of the surface atoms, respectively. The gray spheres and octahedra in the background depict the atomic positions of La/Ba and B in LaB_6/BaB_6, respectively (the lattice spacing in LaB_6 is smaller).

B. Electronic properties

Not only is the termination of the LaB_6/BaB_6 heterostructure with Ba atoms thermodynamically preferred, but it also leads to a lower work function of 1.89 eV as compared to termination with La atoms, which has a work function of 2.30 eV (Table I). The strong driving force for diffusion of Ba to the surface is thus important for maintaining the lowest-possible work function of this material under thermionic emission operation conditions. The Ba-terminated, stable $LaB_6/BaB_6(100)$ surface has a 0.46-eV-lower work function than pure LaB_6 (Fig. 2; the La-terminated heterostructure only has a 0.05-eV-lower work function than pure LaB_6). The work function of the heterostructure is 0.34 eV lower than the work function of $BaB_6(100)$. The Ba-terminated LaB_6/BaB_6 heterostructure thus has a lower work function than both the constituent phases.

TABLE I. Work functions of $LaB_6(100)$ and Ba- and La-terminated $LaB_6/BaB_6(100)$. Both the values for slabs with atoms at bulk positions and relaxed slabs are shown. The Ba-terminated heterostructure has the lowest work function. There is a strong thermodynamic driving force for diffusion of Ba atoms to the surface as described in the text, such that the surface of the heterostructure will be replenished with Ba atoms during thermionic operation.

Structure	Termination	Work function (eV, relaxed)	Work function (eV, unrelaxed)
LaB_6	La	2.35	2.73
BaB_6	Ba	2.23	2.05
LaB_6/BaB_6	La	2.30	2.58
LaB_6/BaB_6	Ba	1.89	1.75

For pure LaB_6, relaxation at the $LaB_6(100)$ surface leads to an inward movement of the terminating La atoms by about 0.3 Å. This relaxation leads to an increase in hybridization between the surface La 6*s*, 5*d* and subsurface B 2*s*, 2*p* states, which form a surface band common to hexaborides due to dangling B bonds [9,12,42,43]. This increase in hybridization due to relaxation can be seen in the increase in DOS at about 2 eV below the Fermi level shown in the top panel of Fig. 3. Despite the inward movement of the surface La atoms, surface relaxation reduces the work function due to redistribution of charge from the surface La atoms to this surface band [9,12,42]. The work function of $LaB_6(100)$ without surface relaxation would be 2.73 eV, the charge redistribution induced by surface relaxation reduces the work function by 0.38 eV.

In the case of Ba-terminated $LaB_6/BaB_6(100)$, the inward movement of the terminating Ba atoms is less than 0.1 Å, and there is little change due to relaxation in the before-mentioned surface band (bottom panel of Fig. 3). In contrast to pure $LaB_6(100)$, the work function increases due to surface relaxation from 1.75 to 1.89 eV, since there is no charge redistribution to compensate the dipole reduction

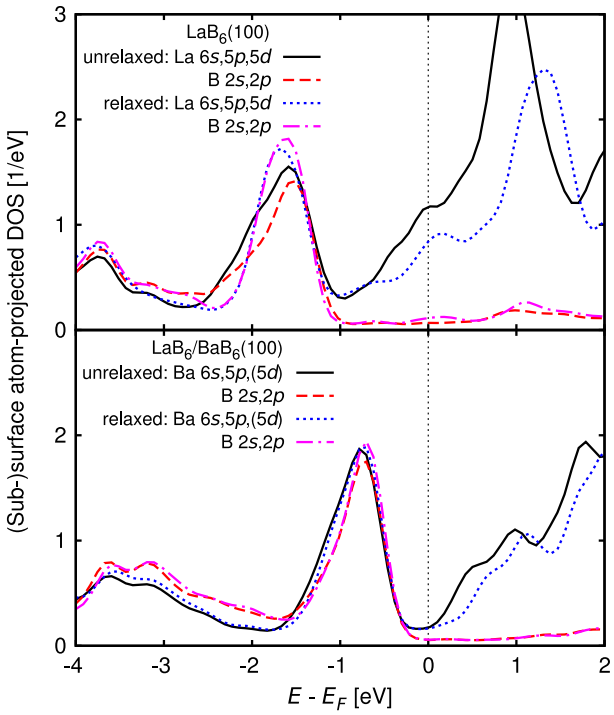

FIG. 3. Surface and subsurface atom-projected DOS for $LaB_6(100)$ (top panel) and $LaB_6/BaB_6(100)$ terminated with Ba (bottom panel). The DOS for both the unrelaxed (atoms at bulk coordinates) and the relaxed structures is shown. At approximately −2 and −1 eV, the DOS shows the surface bands due to dangling B bonds for $LaB_6(100)$ and Ba-terminated $LaB_6/BaB_6(100)$, respectively.

due to the inward movement of the surface atoms. Hence, the electronic mechanism responsible for the work function lowering with surface relaxation in LaB_6 is not active in the Ba-terminated heterostructure. Nevertheless, due to the large ionic radius of Ba, the surface dipole is larger for the Ba-terminated heterostructure to begin with, leading to the 0.46-eV-lower work function compared to $LaB_6(100)$. Generally, as summarized in Table I, both for the heterostructure and the pure hexaborides, La-terminated surfaces experience a work-function lowering due to surface relaxation, and Ba-terminated surfaces experience an increase in work function.

C. Thermionic emission

We calculate thermionic current densities using Eq. (1), considering bulk LaB_6/BaB_6 and LaB_6 as metallic leads and surface slabs of the two materials as scattering regions, respectively.

The thermionic current densities are predicted to be an order of magnitude higher for $LaB_6/BaB_6(100)$ than for $LaB_6(100)$ (Fig. 4). A fit of the current densities to the Richardson-Dushman equation (Φ: work function) [44]

$$J(T) = AT^2 \exp(-\Phi/k_B T), \tag{2}$$

yields a preexponential factor A of ~ 10 A/cm^2/K^2 both for $LaB_6/BaB_6(100)$ and $LaB_6(100)$. Note that, in the definition of Eq. (2), A includes electronic reflection coefficients and to lowest order temperature dependence of the work function [44,45], which itself is considered temperature independent in Eq. (2) and also includes temperature dependence to lowest order. The lowering of the work function in the heterostructure thus does not lower the tunneling amplitudes, in contrast to the effect of dipole barriers in the case of work-function lowering through alkali-metal or alkali-earth-metal adsorption on, e.g., transition-metal surfaces [34].

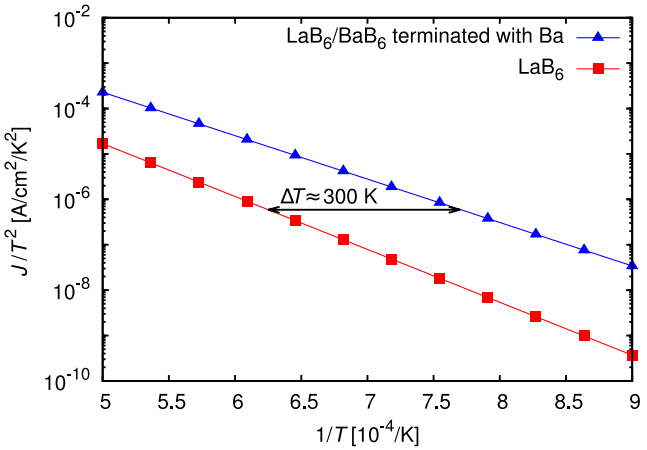

FIG. 4. Richardson-Dushman plot of thermionic emission from $LaB_6/BaB_6(100)$ and $LaB_6(100)$. The arrow indicates by how much the working temperature of a LaB_6/BaB_6 cathode could be lowered, yielding the same current densities as a LaB_6 cathode at higher temperatures.

Hence, the working temperatures for thermionic emission could be lowered significantly with LaB_6/BaB_6 cathodes. To obtain, e.g., the same current density a pure LaB_6 cathode would yield for $T = 1600$ K, the working temperature could be lowered by 300 K with a LaB_6/BaB_6 heterostructure cathode.

IV. CONCLUSION

Based on first-principles calculations, we have shown that cathodes composed of LaB_6/BaB_6 heterostructures have a significantly lower work function than pure LaB_6 cathodes without sacrificing either thermodynamic stability or tunneling amplitudes. The low work function of LaB_6/BaB_6 is an intrinsic property of the structure that does not depend on a work function lowering coating and will be maintained under thermionic emission conditions. The heterostructure cathodes could be operated at much lower temperatures than LaB_6 cathodes, leading to a more efficient cathode with a potentially increased lifetime. The lower work function would also render LaB_6/BaB_6 a more efficient field-emission cathode material than pure LaB_6.

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