PHYSICAL REVIEW B **86**, 035142 (2012)

Anomalous work function anisotropy in ternary acetylides

Joseph Z. Terdik,[1] Károly Németh,[1,*] Katherine C. Harkay,[1] Jeffrey H. Terry, Jr.,[1,2]
Linda Spentzouris,[1,2] Daniel Velázquez,[1,2] Richard Rosenberg,[1] and George Srajer[1]
[1]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
[2]*Illinois Institute of Technology, Chicago, Illinois 60616, USA*

(Received 2 December 2011; revised manuscript received 11 June 2012; published 24 July 2012)

Anomalous anisotropy of work function values in ternary alkali metal transition metal acetylides is reported. Work function values of some characteristic surfaces in these emerging semiconducting materials may differ by more than 2 eV as predicted by density functional theory calculations. This large anisotropy is a consequence of the relative orientation of rodlike $[MC_2]_\infty$ negatively charged polymeric subunits and the surfaces, with M being a transition metal or metalloid element and C_2 refers to the acetylide ion C_2^{2-}, with the rods embedded into an alkali cation matrix. It is shown that the conversion of the seasoned Cs_2Te photoemissive material to ternary acetylide Cs_2TeC_2 results in substantial reduction of its ≈3 eV work function down to 1.71–2.44 eV on the $Cs_2TeC_2(010)$ surface, while its high quantum yield is preserved. Similar low work function values are predicted for other ternary acetylides as well, allowing for a broad range of applications from improved electron and light sources to solar cells, field emission displays, detectors, and scanners.

DOI: 10.1103/PhysRevB.86.035142 PACS number(s): 73.20.At, 65.40.gh, 71.20.Nr, 81.05.Zx

I. INTRODUCTION

For many photophysical applications photoemissive materials are sought after that can turn a high fraction of the incident photons into emitted electrons, that is, materials that have a high quantum yield. Often, the quantum yield of these materials depends heavily on the wavelength of incident photons. For many applications, ranging from electron guns for synchrotrons and free-electron lasers to night vision devices, high quantum-yield photoemission using visible or infrared irradiation is desirable. In electron guns of synchrotrons and free-electron lasers, emission in the visible range is advantageous for the improved control of the shape of the emitted electron bunch that is critical for time-resolved applications. In night-vision devices a very low flux of infrared photons has to be turned into emitted electrons with a high yield in order to obtain an image as sharp as possible. Therefore there is a quest for new and improved materials with optimized quantum yield and low-work function.[1]

Cs_2Te has been known since the 1950s for its high quantum yield[2] using ultraviolet illumination with photon energies above ≈3.0 eV and has been used for many decades as a primary high-yield photocathode. Besides not being photoemissive in the visible region, its other main drawback is that its surface gets oxidized in practical vacuum, whereby its quantum efficiency substantially reduces.[3] Despite this disadvantage, Cs_2Te still has 20–30 times longer operational lifetime than competing multialkali antimonide photocathodes, such as K_2CsSb and $(Cs)Na_3KSb$, especially when operated in radio-frequency accelerating cavities.[3]

In the process of attempting to design modifications of Cs_2Te with lowered work function and preserved high quantum yield, we have considered the effects of small gas molecules on Cs_2Te surfaces. Such effects have been studied by di Bona *et al.*[3] using small gas molecules occurring in vacuum, such as O_2, N_2, CO_2, CO, and CH_4. It occurred to us that the effect of another small gas molecule, acetylene (C_2H_2), has not been considered yet, despite the potentially interesting reactions between C_2H_2 and Cs_2Te. C_2H_2 is widely used for welding (not in accelerators though) and it might occur in accelerator vacuums as well, in trace amounts. It is an acidic compound and prefers to decompose to acetylide anion C_2^{2-} and to $2H^+$ in the presence of a base. Based on the acidic character of C_2H_2, one might investigate the working hypothesis that the reaction of

$$Cs_2Te(cr) + C_2H_2(g) \rightarrow Cs_2TeC_2(cr) + H_2(g) \qquad (1)$$

would produce a ternary acetylide Cs_2TeC_2, whereby the oxidation number of Te would change from −2 to 0 and that of H from +1 to 0, with (cr) denoting crystal and (g) gas phase. Interestingly, the class of ternary (i.e., three-component) acetylides indeed exists, involving already synthesized members with the general formula of A_2MC_2 with $A \in [Na,K,Rb,Cs]$ and $M \in [Pd,Pt]$, and the oxidation number of the metal M in them is zero.[4,5] All existing compounds of the A_2MC_2 formula have a hexagonal unit cell with rodlike $[MC_2]_\infty$ substructures running parallel with the main crystallographic axis, and very similar distribution of alkali atoms around the $[MC_2]_\infty$ rods, just as indicated in Figs. 1 and 2. All known A_2MC_2 materials are colored semiconductors with 2.1–2.8 eV direct band gaps.[5] The other class of ternary acetylides with synthesized members contains only a single alkali atom and has the formula of AMC_2[6] with the $[MC_2]_\infty$ rods adopting three different kinds of rod packings.[7]

II. METHODOLOGY

Adopting the structure of the unit cell of Na_2PdC_2 and substituting Na with Cs and Pd with Te we have carried out a full crystal structure (lattice parameters and atomic fractional coordinates) optimization using density functional theory (DFT), without any symmetry and point group constraints on the translational unit cell. We have used the PWSCF code,[8] plane-wave representation of wave functions with 80 Rydbergs wave function cutoff, the PBE exchange-correlation functional[9] in conjunction with norm-conserving pseudopotentials for Cs, Na, and Te and ultrasoft ones for the other elements as available in the PWSCF distribution. The