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Active bialkali photocathodes on free-standing graphene substrates

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The hexagonal structure of graphene gives rise to the property of gas impermeability, motivating its investigation for a new application: protection of semiconductor photocathodes in electron accelerators. These materials are extremely susceptible to degradation in efficiency through multiple mechanisms related to contamination from the local imperfect vacuum environment of the host photoinjector. Few-layer graphene has been predicted to permit a modified photoemission response of protected photocathode surfaces, and recent experiments of single-layer graphene on copper have begun to confirm these predictions for single crystal metallic photocathodes. Unlike metallic photoemitters, the integration of an ultra-thin graphene barrier film with conventional semiconductor photocathode growth processes is not straightforward. A first step toward addressing this challenge is the growth and characterization of technologically relevant, high quantum efficiency bialkali photocathodes on ultra-thin free-standing graphene substrates. Photocathode growth on free-standing graphene provides the opportunity to integrate these two materials and study their interaction. Specifically, spectral response features and photoemission stability of cathodes grown on graphene substrates are compared to those deposited on established substrates. In addition, we observed an increase of work function for the graphene encapsulated bialkali photocathode surfaces, which is predicted by our calculations. The results provide a unique demonstration of bialkali photocathodes on free-standing substrates, and indicate promise towards our goal of fabricating high-performance graphene encapsulated photocathodes with enhanced lifetime for accelerator applications.

npj 2D Materials and Applications (2017)1:12; doi:10.1038/s41699-017-0014-6

INTRODUCTION

The evolving needs of advanced electron accelerator-based X-ray light sources, such as energy recovery linacs and free electron lasers have motivated continual development in photocathode (PC) materials with a particular emphasis on high brightness and long lifetime.^{1–6} Semiconductor materials, particularly those of the alkali-antimonide family are of keen interest as their relatively high quantum efficiencies, and low thermal emittances can yield a high brightness beam. Their characteristic sensitivity to the local gas environment, however, limits them to short operational lifetimes in most accelerator vacuum environments.¹ This sensitivity is typically due to ion or thermally induced damage at the surface, and can include changes in stoichiometry due to cesium loss, electrolysis, and/or material decomposition. For the general considerations of vacuum sensitivity, studies of quantum efficiency (QE) degradation of the alkali-antimonides have found that the dominant effect is due to surface poisoning through irreversible reactions with residual reactive gases containing oxygen.² Given that graphene has been shown to be impermeable to gas molecules,³ even hydrogen and helium,^{4–6} a goal of this study is to examine the feasibility of utilizing graphene as an

atomically flat, ultra-thin barrier to passivate the sensitive PC surface and prevent degradation in photosensitivity.⁷ The ability to control the number of layers and grow relatively large area (e.g., $\sim 1 \text{ cm}^2$) graphene thin-films using chemical vapor deposition (CVD) provides a path for investigating the protective barrier properties.^{8,9} Additionally, limiting the thickness to a few atomic layers can preserve transmission of the photoexcited electrons into vacuum. A critical first step in investigating the barrier properties of graphene is the ability to mechanically and electrically interface the PC with graphene while not compromising the PC through thermal decomposition or contamination. Synthesis of graphene requires high temperature and pressure of precursor gases, while the synthesis of the bialkali PC (K_2CsSb) requires relatively lower temperatures and extreme vacuum purity. Bringing these compounds together required an innovative “top-down” approach, wherein ultra-thin few-layer graphene was separately grown and then suspended on a nickel-mesh scaffold. The bialkali cathode was then grown on the suspended graphene substrate in the open areas of the nickel mesh.

Using this suspended substrate method, we measured a QE (the ratio of the number of emitted electrons $\Delta Q/q$ to the number of incident photons $\Delta E/\hbar\omega$, or $\text{QE} = (\hbar\omega/q)(\Delta Q/\Delta E)$) exceeding 5% at

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Received: 13 October 2016 Revised: 20 January 2017 Accepted: 1 March 2017

Published online: 01 June 2017

the vacuum surface of the PC grown on few layer graphene, which demonstrates the potential to grow state-of-the-art alkali PCs with quantum efficiencies in the accepted range of 1–10% grown on well-characterized bulk substrates.^{1, 10} This strategy overcomes the complications that could arise using the conventional ‘bottom-up’ approach using a in-vacuo dry transfer technique, which remains a challenge to (a) secure an approximately mm-range defect-free area suitable for PC applications, and (b) execute the transfer in pristine vacuum. Moreover, our approach demonstrates the feasibility of PC synthesis on free-standing ultra-thin substrates, which may be of use in adjacent applications. We observe an increase in effective work function of the PC at the graphene interface, and this is compared to theoretical calculation results. Validation of graphene-cathode compatibility, as evidenced by stable photoemission (from both the coated and uncoated sides) and correlated perturbation of spectral response, opens new avenues to cathode designers. In particular, it demonstrates, for the first time, the critical functions of charge injection, charge extraction, mechanical support, and optical transparency in the entirely new configuration of free-space suspension of cathode films on few monolayer substrates.

RESULTS AND DISCUSSION

Overall concept and measurement setup

The design of free-standing graphene substrates on mesh grids as shown in Fig. 1a provides a unique opportunity to probe photoresponse from both sides. This is critical for studying the effect of the graphene substrate on the PC performance, as will be discussed in the next subsection. The schematic in Fig. 1a depicts the overall concept, where a 2- μm thick nickel mesh grid with unit cell aperture of 6.5 μm and open area $\sim 42 \mu\text{m}^2$ is used to suspend a graphene substrate with thickness between 5–8 monolayers. Figure 1b shows the arrangement for photocurrent measurement:

a patterned anode is deposited on the inside of the windows, which preserves transparency while facilitating electron collection; the excitation laser can be easily positioned within the patterned anode material to impinge upon the active cathode area at a desired location. Photocathode deposition occurs on the nickel (Ni) mesh side of the graphene substrate, such that the mesh functions as the charge injection electrode. For PC characterization, a vacuum-sealed package was devised with optically transparent sapphire windows on both sides of the PC. The sealed construction is similar to that of a commercial phototube, and allows for long-term storage and study. Photoelectrons emitted from the desired surface are measured using a low-noise nanoammeter while a bias voltage is applied to charge-collecting anodes (Fig. 1b, see Methods section for details). Figure 1c shows an end-view of the setup with a red circle indicating a representative optical spot.

Photocathode deposition on free-standing graphene substrates

Graphene films of five and eight-layer thickness (5 and 8L hereafter, respectively) were prepared as free-standing substrates to investigate the performance of bialkali antimonide PCs. Monolayer graphene was stacked via transfer process instead of direct multilayer growth to achieve high reproducibility and controlled thickness (see Methods section for details). The graphene used in this study was grown by CVD method on copper (Cu) substrates. The graphene quality was tested using Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM), following a well-established wet-transfer process¹¹ on Si/SiO₂ substrates. Characterization results indicated that the transferred monolayer graphene had minimal crystal structure defects on the scale of $\sim 1 \mu\text{m}$, and thickness was $\sim 0.5 \text{ nm}$. Specifically, Raman spectra for the film exhibited two dominant peaks of G and 2D, around ~ 1580 and $\sim 2700 \text{ cm}^{-1}$, respectively, and absence of D peak around 1350 cm^{-1} (Fig. 2a).

Fig. 1 **a** Concept of graphene substrate PC. **b** Schematic of experimental setup. **c** Photograph of graphene substrate PCs sealed in a vacuum tube. Red circle indicates an optical spot size used for the measurements

The D peak is indicative of defects or discontinuities in the carbon network because the A_{1g} zone-boundary Raman mode of carbon atoms requires their presence. An absence of this vibrational mode is indicative of high crystal quality. Raman spectra can also be used to identify the thickness of graphene using the ratio between the heights of the 2D and G peaks. The value for our graphene was $2D/G \sim 3$, which is well above an accepted characteristic value of 2 for monolayer graphene.¹² The thickness of the monolayer graphene was further confirmed by cross-sectional height profile using AFM, revealing a height of ~ 0.5 nm (Fig. 2b). In addition, AFM studies confirmed a smooth and flat surface of monolayer graphene without observable pinholes or ruptures, which are consistent with the Raman results indicating minimal structural defects in this film (see Fig. 2c, where scale bar is 1 μ m). The uniformity of monolayer graphene for broader regions was confirmed by SEM (see [Supplementary Information](#)).

Nickel mesh transmission electron microscopy (TEM) grids with a mesh aperture of 6.5 μ m were used as a supporting scaffold for the 5 and 8L graphene substrates. As previously mentioned, TEM grids instead of rigid substrates were used to allow for subsequent deposition of bialkali cathode material on graphene in a manner that would allow for photoemission from both the graphene-coated and uncoated sides. A wet-based process was used for transfer of graphene to the TEM grids¹¹ (see Methods section for details). Figure 2d shows optical microscope images of as-prepared 8L graphene substrates (scale bar is 100 μ m), and optical microscope images of the TEM grid without graphene are shown in [Supplementary Information](#) for comparison. It is clear that very thin graphene sheets are able to span the mesh holes with 6.5 μ m

diameter without observable pinholes or ruptures. Reliably spanning the open area of a TEM mesh is itself a practical confirmation of the transfer process. Nearly 100% coverage of the 2 mm diameter TEM mesh grid was confirmed for 5 and 8L graphene substrates using optical microscopy (see [Supplementary Information](#) for details).

For the PC deposition, the TEM grid-supported graphene substrates were assembled onto a pre-cleaned stainless steel (SS) outer frame assembly in a 3×3 array structure (see [Supplementary Information](#)). The graphene substrates in the assembly were oriented such that the PC was deposited on the exposed Ni mesh side in order for the Ni mesh to act as the charge injection electrode. Photoemission current was monitored as a process metric during deposition using a SS witness substrate, and the stoichiometry of typical resulting PC films using this process has been previously confirmed as K_2CsSb .^{13, 14} The entire frame assembly was then sealed in a vacuum package using conventional phototube techniques. The specially designed vacuum package also integrates the aforementioned anode grid patterns on the sapphire windows. The grids and the cathode are all electrically floated with respect to the chassis of the tube and this arrangement minimizes leakage current between the PC and the anodes (see [Supplementary Information](#)). This type of vacuum-tube PC enclosure provides an extremely stable environment for long-term experiments (much longer than what is observed in a dynamically pumped vacuum environment).

Photoemission measurements

Validation of graphene-PC compatibility was performed by measuring the QE as a function of wavelength (spectral response) of PCs

Fig. 2 Graphene substrate characterizations by **a** Raman spectroscopy, **b** AFM height profile, **c** AFM topology and **d** optical microscopy. Height profile in **b** is along the dashed line in **c**. Scale bars in **c** is 1 μ m, **d** is 100 μ m

deposited on 5 and 8L graphene substrates. Of the four possible combinations of incident light “in” and photoemission current “out” as indicated in Figure 1a (i.e., PC-in/graphene (Gr)-out, PC-in/PC-out, Gr-in/PC-out, Gr-in/Gr-out), the spectral response from the Gr-in/Cs-out configuration (transmission mode) was found to provide the most useful method for studying K_2CsSb deposited on graphene substrates. The reason is that only minimal and reliable corrections are required to obtain absolute QE values (see [Supplementary Information](#) for details). Figure 3a shows the spectral response in this configuration for the PCs deposited on 5 and 8L graphene substrates, where persistent photoemission was achieved with peak QE of 5.69% at 3.14 eV (395 nm) and the spectral response exhibited characteristic features similar to that of K_2CsSb reference cathodes (indicated by the *purple arrows*). Graphene transmission loss of 2.3% per monolayer is taken into account. A QE value exceeding 5% in the UV from K_2CsSb PCs on free-standing few-layer graphene substrates provides a clear demonstration of PC-graphene substrate architecture as a promising high QE PC with enhanced lifetime and chemical robustness^{1, 10, 13} as has been sought since the emergence of PCs as a bunched electron source for injectors.¹⁴ It should also be noted that the peak in QE between 3–3.5 eV evident in Fig. 3a is a general characteristic shared among the family of the alkali antimonide PCs. The primary cause is an onset of electron–electron (e – e) collisions: e – e scattering events are prevented until the final states of both electrons can reside in the conduction band of K_2CsSb .¹⁵ This means that for photon energies below the observed peak in QE, electrons excited from the top of the valence band, for example, do not have enough excess energy to scatter with another electron (because their final states would lie within the bandgap). This leaves phonon scattering as the only scattering mechanism and QE continues to rise with increasing incident photon energy until the final states of two collisional electrons can both lie in the conduction band. This region corresponds to 3.0–3.5 eV for alkali antimonides, and QE drops even as incident photon energy increases (as seen in Fig. 3a). Another contributing factor to the peak QE in the region of 3.0–3.5 eV is that optical absorption is highest in this region (as demonstrated in Fig. 3b), as is optical penetration depth. The resulting shape and fine structure of the spectral response curve is therefore unique to the particular film in question (e.g., with a particular stoichiometry, crystallinity, thickness). The nearly perfect match between the spectral response curves in Fig. 3a, corresponding to 5 and 8L graphene substrates, eliminates the possibility of graphene substrate thickness dependence on the intrinsic response of the deposited K_2CsSb PCs. Recall that the method for preparing graphene substrates (see [Supplementary Information](#)) allows unambiguous differentiation between 5 and 8L. The similar behavior of K_2CsSb PCs on 5 and 8L substrates is further

supported by optical transmittance: both cases showed weak features corresponding to the signature peaks (indicated by the *purple arrows* in Fig. 3b) and lower transmittance for 8L is consistent with a stronger absorption within a thicker graphene substrate. These PCs are highly stable in the vacuum-sealed phototube environment indicating no long-term adverse reaction between the K_2CsSb and graphene substrates. Similar to a reference PC region deposited on the SS frame assembly there was no observable decrease in QE over a 100 min stability measurement during current extraction from the PCs on the graphene substrates (Fig. 3c). Furthermore, no degradation was observed over a 6+ month period since the time of the PC fabrication.

Despite the demonstrated functionality of K_2CsSb on graphene substrates, the resulting QE is lower at all wavelengths compared to that obtained using conventional bulk substrates. For instance, transmission-mode K_2CsSb on glass or sapphire bulk substrates can exhibit peak QE in excess of 25% in the region of ~3.5 eV ([Supplementary Information](#)). Within the tube assembly, a significantly higher QE was obtained from the PC film on the SS reference regions than on the graphene substrates. The suppressed spectral response could be caused by a number of factors. A likely hypothesis is an initial presence of residual water molecules on the graphene substrates. This is unlikely for conventional bulk substrates given the extended high-vacuum bakeouts utilized in industrial PC production, however in the case of few-layer graphene substrates a trace amount of adsorbed water molecules could remain trapped in between the layers during their wet-based stacking processes and present a local source of contamination to the PCs. This could be particularly true in this study due to the fact that the suspended graphene was not subjected to a prolonged anneal. The graphene substrates were thermally annealed at only 100 °C in air after each of the transfer steps to minimize trapped water at the interlayer. However, an in-vacuum anneal is required to eliminate the possibility of residual water and this study is planned for the near-future. Earlier investigations have shown that residual water can persist even during thermal annealing at 350 °C in ultra-high vacuum (UHV), due to their geometrical capping by the graphene basal planes.^{16–18} From optical transmission measurements, the K_2CsSb film thickness on graphene substrates were estimated to be similar to that obtained on conventional substrates under similar growth conditions (>20 nm), suggesting that differences in adhesion coefficients and the resulting film thicknesses play a minimal role in the observed QE difference over conventional substrates. Spectral features in optical transmission of the K_2CsSb films were observed to be less distinct on graphene compared to that of reference deposited on sapphire substrates ([Supplementary](#)

Fig. 3 **a** QE spectral response, **b** Optical transmission, **c** Stability of K_2CsSb PCs deposited on graphene substrates. For **a** and **b**, red circles and black squares are for the PCs on 5 and 8-layer graphene substrates, respectively. Purple arrows indicate the regions with signature features. Black line in **c** is for a PC on SS substrate as a reference, and purple line is for PC on 8-layer graphene substrate. QE is normalized in **c** to the PC on SS substrate

Information). This may be an indication of K_2CsSb film degradation due to the presence of the graphene substrate, or vice versa, and details are to be investigated in a follow-on study. Regardless, the deposited PC exhibited QE that exceeds 5%, demonstrating that the critical function of charge injection, charge extraction, and mechanical support were satisfied in entirely new configurations of free-space suspension of bialkali PC films on few monolayer substrates.

The validation of graphene-PC compatibility and functionality was further investigated by studying the photocurrent emitted on the graphene side. The measurements provide insight on the PC performance at the graphene interface in contrast to the photoemission obtained from the non-graphene side. It is worthwhile noting again that graphene is one of the very few material options available for this purpose, if not the only one: it satisfies all requirements of being optically transparent and providing a mechanically stable support, while prior studies of monolayer graphene on planar Cu PCs have shown that the graphene barrier does not significantly block electron transport (tunneling) through it¹⁹ as part of the so-called “three-step” photoemission process.²⁰ For this study of Gr-side electron emission, the cathode was illuminated from the back (Gr) side (illumination from the K_2CsSb (PC) side could also provide information about PC performance at the graphene interface, albeit in a less direct manner). Photoemission was indeed observed from the graphene side, and including the necessary optical corrections (Supplementary Information) the QE was measured at $\sim 1.0\%$ at 4.5 eV, significantly lower than for direct photoemission into vacuum (i.e., emitted to the PC side) for the

same sample as indicated in Fig. 4a. Furthermore, drastic changes in the spectral response features were observed as shown in Fig. 4b, suggesting a change in the electronic structure of K_2CsSb at its interface with graphene (to be discussed in comparison with our calculation results). To gain insight into the change that would impact the PC performance, we examined the work function of this K_2CsSb -graphene system. The effective work function can be determined by observing the low-energy cutoff of Fig. 4b. Specifically, this data was re-plotted using the square root of QE for the vertical axis, and the linear region of the data was extrapolated to the horizontal axis as shown in Fig. 4c.^{2, 21} The results indicate that the work function increased by ~ 0.3 eV (Fig. 4d) compared to the direct photoemission (PC) side, where the cut-off energy was consistent at ~ 1.8 eV regardless of substrate thickness. These results suggest that while there appears to be a drastic change of K_2CsSb electronic structure at the graphene interface, it does not affect the electronic structure on the vacuum-interfacing side of the PC film, which has estimated thickness of >20 nm. Considering the electron escape depth for the energy range of incident photons, the thickness of K_2CsSb with intrinsic electronic structure can be estimated to be more than ~ 10 nm.²²

Importantly, the lower QE observed from Gr-side photoemission (compared to that of PC-side) agrees with theory prediction, but the cause of apparently negligible difference in QE between the 5 and 8L graphene substrates remains unclear. If the collected photoelectrons are originating from K_2CsSb via tunneling through graphene, the expected result would be a strong dependence on graphene thickness correlated to QE. Quantum tunneling

Fig. 4 QE spectral response based on photoemission from the PC and graphene (Gr) sides of the films. GrPC indicate photoemission measured in a Gr-in, PC-out configuration and GrGr in a Gr-in, Gr-out configuration. **a** QE (%) vs. incident photon energy. **b** QE normalized to the highest value from the PC side. **c** Photon energy cutoff indicating the work function. Extrapolating lines are shown in dash. **d** Work function of the PCs deposited on the graphene substrate with different thicknesses. Gr thickness = 0 is for PC deposited on SS as a reference

introduces an exponential decay in the transmitted current that scales with the product of the barrier width with the square root of the barrier height above the electron energy level²³ (there is ~1.5 nm thickness difference between the thickness of 5 and 8L). However, the Gr-side QE for K_2CsSb had the same order of magnitude for both 5 and 8L, suggesting that a simplistic notion of tunneling through graphene is not a sufficient description. An alternate explanation of the similarity in response for the case of 5 and 8L is the possibility of diffusion of element(s) through free-standing graphene substrates to the non-deposited side during PC deposition, which we observed for a case of Cs_3Sb (Supplementary Information). Cs is an element with known high diffusivity thus it is useful to consider the possibility that the Gr-side photosensitivity originates from PC material, which diffused through the graphene layer during fabrication. Note, however, that the shape of the spectral response curve for photoemission from the graphene side does not resemble that of the reference sample or that from the opposite side. Thus, if photosensitivity is due to diffusion, the diffused material does not share the same stoichiometry as K_2CsSb . Possible diffusion paths of Cs could be either at macroscopic in-plane structural defects of graphene or narrow cracks at the edges of PC films. A counterpoint to this explanation, however, is that the resulting layer would likely be

very thin and not able to account for the comparatively large photocurrent observed. Although the interface between graphene and diffused PC material could still provide information on electronic structure, the limited amount of diffused photosensitive material on the non-deposited side of graphene may be the origin of the observed Gr-side photoemission. In the planned follow-on study, graphene substrates will be prepared with much fewer macro-scale structural defects ($>5\mu m$) (which may be induced during the transfer process) such that permeation of alkali material would be significantly reduced or eliminated entirely.

Density functional theory (DFT) calculations for band diagram at the interface

An increase in work function for K_2CsSb by the presence of interfacial graphene is indeed found in our calculation results, as discussed below. To perform the calculations, significant expansion of the unit cell for graphene was required, namely its 7×2 reconstruction and appropriate resizing of the K_2CsSb (111) unit cell to match their lattices. A Cs-rich surface was chosen beneath graphene, as recommended by experiment, and graphene was placed symmetrically on both sides of the slab resulting in a total cell stoichiometry of $(K_8Cs_7Sb_5C_{28})_2$. This reflects 13 layers of

Fig. 5 **a** Unit cell of graphene on K_2CsSb , with C, Cs, K, Sb atoms shown as black, blue, red and yellow, respectively. Views are shown along [111] direction (left) and (111) planes (right). **b** The local electrostatic potential without (left) and with (right) graphene on the surface of K_2CsSb . All curves are averaged over the directions transverse to the surface normal. The red curve shows a suitable macroscopic average over approximately 5 Å to demonstrate the energy zero level, relative to vacuum. Inset is enlarged. **c** Direction of dipole at graphene- K_2CsSb interface. Blue and red regions indicate electrons are being lost and gained, respectively. Specifically, electrons are being lost from the Cs atoms (regions indicated by black circular lines), and are gained by the C atoms (red honeycomb regions). **d** Band diagram at graphene- K_2CsSb interface with inputs from **b** and **c**

K₂CsSb slab between two layers of graphene, and a vacuum layer of at least 10 Å. The sandwiched structure was required simply for the calculation procedure purpose, and Fig. 5a shows the unit cell for graphene on K₂CsSb (111) from two views that correspond to the experiments described herein. To calculate the work function, the Fermi energy is subtracted in each case from the value of the electrostatic potential in the vacuum region. The electrostatic potentials, or rather pseudopotentials (from the VASP distribution), are depicted in Fig. 5b. The energy zeroes and vacuum electrostatic potential differ in the calculations depending on whether graphene is present or not, but energy differences, such as the work function, are well-defined and give the values of 1.75 and 3.70 eV by interfacing it with and without graphene, respectively. Notably, graphene presents a delta function-like well potential that scatters states transmitting from the bulk in a similar fashion as for potential barrier tunneling. A working theory for the change in work function and/or Fermi level is that electronegative adsorbates tend to increase the work function, although there are exceptions to this rule.²⁴ Adsorbates that are more electronegative than the substrate cause electrons to transfer to the adsorbate layer, causing an excess of negative charges on the outside and an excess of positive charges on the inside of the surface. This leads to a negative dipole pointing inward that reinforces the original surface dipole, causing the work function to increase. Cs is the most electropositive element thus we can expect electron transfer to the graphene, causing the work function to increase. The directions of the dipole at the K₂CsSb-Graphene interface, based on above mentioned explanation, is consistent with our calculation results as shown in Fig. 5c.

The significance of these calculations is as follows. First, there is a charge transfer between the bulk K₂CsSb and the graphene layer, indicating that the graphene layer is n-doped. Second, there is a change in the Fermi level of the graphene layer that translates to a change in the work function level of the graphene as a consequence of n-doping by the bulk K₂CsSb. This results in a reduction of work function for a single layer of graphene from 4.5 to 3.7 eV,²⁵ that is higher than the work function of 1.75 eV for the bulk K₂CsSb (see Fig. 5d); this partially accounts for the changes in work function observed experimentally. Third, as evident from Fig. 5b, short range features exist in the potential that affect transport, the details of which will be studied separately. Figure 4c shows how the interactions described above (between graphene and the adjacent K₂CsSb layer) affect photoemission. Namely, emission from the PC-side of graphene shows no difference in QE and work function between the 5 and 8L cases, suggesting that for PC-side emission the charge transfer at the interface does not play a role because the electronic structure of K₂CsSb remains the same far from the interface. It is reasonable to assume this conclusion is valid for arbitrary layer thickness, so long as mechanical integrity is preserved. On the opposite Gr-side, however, the interface does play a role and so work function increases compared to that of native K₂CsSb and then it further increases from 5 to 8L. This trend of increased work function with increased layer thickness should be expected to continue for thicker graphene substrates. Substrates having fewer than 5L will be investigated in the future.

In general, PCs are sought which operate with the maximum possible wavelength permissible within total charge per bunch and emittance constraints. Unfortunately, these tend to oppose each other (both QE and emittance generally increase as wavelength decreases)²⁶. Particular wavelengths depend on the nature of the drive laser used, whether higher harmonics are generated through frequency doubling crystals, and how the graphene layers affect emission. A reasonable expectation, therefore, is that some optimization would be possible with regard to the wavelength chosen, and such questions will be part of the follow-on study.

Summary discussion

A technologically relevant, active PC film (K₂CsSb) has been grown and characterized on a novel substrate: suspended free-standing few-layer graphene. This was accomplished in an encapsulated package, which allows for long term storage and characterization. The changes in electronic structure were modeled and compared to experimental results. While there is an observed suppression in QE for films grown on 5 or 8 layer graphene, compared to films in this study which were grown on metallic substrates, the response is still well within the accepted 'active' range reported in the literature for alkali-antimonide cathodes grown on conventional substrates (see Fig. 1 in ref. 1). A vanishingly thin substrate, such as graphene, can be expected to introduce multiple effects ranging from mechanical strain to compromised conductivity and charge injection into the film to potential trace contamination of water. These possibilities have been discussed in light of planned follow-on studies. The likely scenario of water molecules being introduced to the K₂CsSb film will be studied further: anneal of the graphene substrates and its fixturing will occur prior to growth deposition for comparison. The results herein demonstrate a PC grown on a novel substrate with immediate and practical utility because its QE as a function of wavelength falls within the accepted ranges for the family of alkali antimonide emitters. The growth of K₂CsSb on a novel substrate is the principal emphasis of this report and it demonstrates significant potential for new technical approaches, such as gas barrier encapsulation, electron energy filtering, and transmission mode PCs, that were not otherwise possible and which could address long-standing challenges.

METHODS

Graphene synthesis and characterization

Cu foils with size of 25 × 75 mm were placed in a quartz tube furnace and pre-cleaned under hydrogen gas flow at 1000 °C for 30 min. Methane gas was then introduced into the tube for 15 min for graphene growth. After being cooled down to room temperature under vacuum, graphene was transferred onto SiO₂/Si substrates (using the aforementioned wet-transfer technique) for material characterization by Raman spectroscopy and AFM (Fig. 2). A WiTec Alpha 300 R spectrometer with 532-nm excitation was used for Raman spectroscopy. The laser spot size was less than 1 μm, and the power was reduced to prevent damage to graphene during the measurements. An atomic force microscope (Veeco Enviroscope) operated in tapping mode with standard cantilevers (tip curvature <10 nm) and spring constant of 40 N/m was used for AFM analysis.

Preparation of free-standing graphene substrates

Poly(methyl methacrylate) (PMMA) was spin-coated on the top side of graphene-grown foils at 4000 rpm for 60 s (MicroChem 495PMMA C4). After pre-bake of the PMMA-support at 180 °C for 3 min, the entire specimen was immersed into Cu etchant of CuSO₄ and HCl aqueous solution for 12 h. After the Cu foils were completely etched away, PMMA-supported graphene was rinsed in a water bath three times, and sized into 3 × 3-mm pieces for transfers. The monolayer graphene was then transferred onto SiO₂/Si substrates for stacking. The transfer process was repeated 5 or 8 times (for 5 and 8L, respectively). After each transfer, the PMMA-support was removed by immersing the entire specimen into an acetone bath heated to 60 °C. A fresh acetone bath was prepared after 15 min and repeated three times, followed by an alcohol (IPA) bath at 60 °C for 15 min. The PMMA-removed monolayer graphene was dried using an air blower and heated to 100 °C for 5 min after each transfer to minimize residual water adsorption. Stacks of 5 or 8L graphene were then coated with PMMA-support for a final transfer onto 2000 line per inch TEM Ni mesh grids (Ted Pella Inc. G2000HAN, 3-mm diameter, 2-μm thickness, hole width 6.5 μm, open area 41%) using the procedures mentioned above. Intermediate transfer onto rigid substrates for a stacking was crucial for increasing the transfer yield. PMMA-supports on TEM mesh grids were removed using the above mentioned procedures of three acetone baths, one IPA bath, and hot-plate annealing at 100 °C.

Bialkali antimonide PC deposition

Graphene substrates on TEM Ni mesh grids were assembled into $55 \times 3 \times 3$ array frames for bialkali antimonide PC deposition and vacuum-tube sealing at PHOTONIS USA. Thin SS foils with hole sizes of 1.5 mm diameter were used to retain the 2 mm diameter TEM grid supports, while some of the 3×3 array frames were left blank to allow reference PCs deposited on SS. The outer frames were electropolished and pre-cleaned along with the foils, including a 600 °C bake in high vacuum. The assembled frames with graphene substrates and all vacuum envelope components were baked at 350 °C in UHV prior to in-situ PC deposition. The PC components K, Cs and Sb were deposited on the SS, and graphene substrates via thermal evaporation to achieve typical stoichiometry of K_2CsSb with thickness of ~25–30 nm generally achieved on the SS. The vacuum package consisted of sapphire windows on both sides of the PC assembly with metal anode traces patterned on the inside of the windows to establish the necessary electric field for photoemission collection and measurement.

Photoemission measurements

A Newport 150 W xenon (Xe) lamp with Oriel CS130 monochromator was used as a light source for photoemission measurements. Optical lenses were used to focus the spot size of incident light to ~1.5 mm, which is compatible with the graphene-spanning regions of the TEM support grids. The incident light was precisely aligned to the desired position in the 3×3 array to prevent stray light from impinging upon neighboring photo-sensitive regions.

Both anode patterns were biased with respect to the PC assembly to extract photocurrent on each respective side, where the photocurrent was collected and measured. It was confirmed that an applied bias of 90 V was enough to overcome space-charge effects and collect photoelectrons in this experimental setup (see [Supplementary Information](#) for details). A 1-M Ω resistor was connected to the SS outer frame support of the PC-deposited graphene substrates using a shielded coaxial cable, and a precision voltmeter was used to measure the voltage across the resistor (i.e., pico-ammeter) to obtain the photoemission current. The QE was calculated using the known power of incident light at each wavelength, as obtained from a calibrated reference diode. The energy of the incident light was scanned from 2 to 4.5 eV while the corresponding photocurrent was recorded to obtain spectral response of the PCs.

DFT calculations

DFT calculations were performed considering an ideal system for the purposes of examining certain qualitative features of the graphene- K_2CsSb interface. The ideal system, in contrast to the experimental configuration, was modeled as a symmetric arrangement of two layers of graphene around a layer of K_2CsSb for computational feasibility. Electronic structure calculations were done using the Vienna Ab initio Simulation Package (VASP)^{27–29}, including core state effects via the VASP implementation³⁰ of projector augmented-wave methods.³¹ We used the local density approximation (LDA)^{32, 33} to DFT,^{34, 35} which is the most basic functional available in VASP. In DFT packages, there are a myriad of functional choices; particularly, geometry/lattice-constants present large differences between generalized-gradient, van der Waals-corrected and other hybrid functional calculations, compared to the LDA. This has been discussed in previous studies on graphene,³⁶ as well as on other metallic^{37, 38} and dielectric systems.³⁹ In the present study, however, LDA provides the superior method for calculating work-function, at least for comparisons to experimental values for elemental surfaces.⁴⁰ LDA also provides a correct graphite interlayer spacing and surface bonding distance. For this reason, we consider herein only LDA functionals. We used the VASP-supplied LDA potentials for C, Cs, K, Sb (specifically, Sep 2000, Mar 1998, Feb 1998 and May 2000 potentials, respectively) from the VASP distribution. All calculations use a kinetic energy cutoff of 500 eV, which is 20% larger than the suggested cutoff for Carbon (400 eV). Generally the cutoff might be chosen higher for a better converged surface energy, but the work-function itself was seen to depend very little on cutoff value. For all structures, a Monkhorst-Pack k -point grid⁴¹ with spacing between 0.2 and 0.3 per Å was chosen, adjusted to ensure a k -mesh consistent with the original unit cell symmetry. As an example, applying these settings, graphene in its primitive cell would use a $15 \times 15 \times 1$ mesh. The k -mesh is forced to be centered on the gamma point. The MedeA software system⁴² was used to drive VASP in calculations of the optical properties, electrostatic potential, and some other calculations.

ACKNOWLEDGEMENTS

Authors acknowledge financial support from the Los Alamos National Laboratory (LANL) Laboratory Directed Research and Development (LDRD) Program through Directed Research (DR) “Applied Cathode Enhancement and Robustness Technologies (ACERT)” (Project #20150394DR). Studies were performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. LANL, an affirmative action equal opportunity employer, is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Authors also acknowledge Charudatta Galande of Rice University and Akhilesh Singh of LANL for their experimental supports on CVD graphene growth.

AUTHOR CONTRIBUTIONS

N.A.M. conceived the project. H.Y. organized the project with supports from N.A.M. H. Y., N.A.M., and A.D.M. designed the experiments. H.Y. prepared graphene substrates. J.D. fabricated bialkali PCs on graphene and sealed them in a vacuum tube. F.L. performed photoemission measurements of PCs and AFM on graphene. C.W.N.V. performed Raman spectroscopy on graphene and arranged XPS measurements. D.F. performed DFT calculations with inputs from A.S., K.J., M.M., and S.L. F.L. and V.P. deposited bialkali PCs on graphene for material characterization. A.D.M. and G.G. oversaw the graphene related efforts. H.Y. wrote the manuscript with supports from N.A.M. and inputs from all authors.

COMPETING INTERESTS

N.A. Moody owns a patent on the concept of graphene protection of chemically reactive films. The other authors declare that they have no financial competing interests.

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Supplementary Information accompanies the paper on the *npj 2D Materials and Applications* website (doi:10.1038/s41699-017-0014-6).