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ENCAPSULATION OF PHOTOCATHODES USING HIGH POWER PULSED RF SPUTTERING OF hBN*

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Abstract

Photocathodes of various materials are used in photoinjectors for generating high quality photoelectron beams. Of particular interest are the alkali antimonides because of their ultra-high quantum efficiency (QE), and metallic materials such as Cu and Mg which have lower QE but have considerably longer lifetime. The biggest challenge of using the alkali antimonide photocathodes is that it has a stringent requirement on vacuum because they are destroyed rapidly in air. Exposure of Mg and Cu in air also impacts their performance because of the oxidation. These photocathodes can be protected by encapsulating them with thin layers of 2D materials such as hexagonal boron nitride (hBN). In this paper, we will discuss the numerical modeling of the encapsulation, the QE measurements of encapsulated Cu as examples, and the feasibility of coating a photocathode with hBN by using high power pulsed reactive RF sputtering.

INTRODUCTION

Background

Alkali antimonide photocathodes are commonly used in high-brightness photoinjectors because of their ultra-high quantum efficiency (QE) at green light wavelength, small thermal emittance and relatively-low requirements for growth. One of the challenges of using the photocathode is that it has an extremely stringent requirement on the vacuum and can be destroyed by even small amounts of reactant gas, including O_2, H_2O, and so forth [1–3]. Meanwhile, the QE of metallic photocathodes like Cu and Mg that are more resilient to air also degrade over time in operations due to oxidation. However, the material and labor costs of building UHV photocathode transferring and storage systems to extend the lifetime of these photocathodes are very high.

Researchers have been exploring the feasibility of encapsulating photocathodes with thin-film materials to increase their lifetime and robustness against air. Previous research have studied thin-films of dielectric materials such as NaI, CsI, etc. [4]. However, the implementation was discontinued due to limited protection and spectral response [5]. Further research was done with thin-films of 2D materials, such as graphene (Gr) and hexagonal boron nitride (hBN). Theoretical modeling and simulations indicate that a monolayer of Gr or hBN can inhibit the photocathode material's reaction with the residual gas, while maintaining its high QE [6].

Our Methods

There are mainly two ways of generating a thin-film of 2D materials directly on a substrate. One is to make a "wet transfer" of the thin-film already grown on a base substrate like a copper foil onto the destination substrate. This method is not applicable for alkali antimonides, as the photocathode needs to stay in a UHV environment after being made, while the transfer requires the substrate to be operated in air and submerged in water. The other method is to directly grow the 2D thin-film on the substrate, which could be achieved via either a chemical vapor deposition (CVD) or physical vapor deposition (PVD). CVD growth of Gr and hBN requires a complex setup and substrate heating (to 750° or higher [7]) and therefore are logistically and physically infeasible.

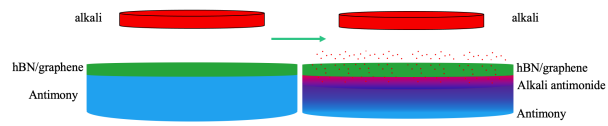

Figure 1: An illustration of the alkali intercalation process.

Recently, authors of this paper have been investigating a novel method to indirectly generate a 2D thin-film on alkali antimonides. In our approach, a process called intercalation is utilized where the alkali atoms penetrate a 2D thin-film of Gr or hBN on an antimony (Sb) coated silicon (Si) substrate to generate alkali antimonides. A conceptual illustration is shown in Fig. 1. We prepared the experimental samples by doing wet transfers of Gr monolayer thin-films on Sb coated Si wafers, denoted as Gr/Sb/Si, and heat treating the Gr/Sb/Si. Characterizations of the samples before, during and after the intercalations done at the NSLS-II beamlines of BNL indicated that Cs_3Sb structures were formed underneath the Gr monolayer. The results of the work are being submitted as a journal publication.

In this paper, we discuss the feasibility of using high power pulsed (HPP) reactive sputtering, which is a PVD method, to generate an hBN thin-film on a photocathode. We first show the density functional theory (DFT) simulations of an encapsulated Cu (111) substrate, and demonstrate the encapsulation protection effect by comparing the QE of naked and encapsulated Cu substrates. The instrumental setup of the HPP sputtering system is then presented and characterizations of the sputtered boron nitride thin-films are shown.

DFT SIMULATIONS

Density functional theory (DFT) was developed in the 1960's to calculate the electronic structures of materials and provide fundamental insights for properties such as adhesion,

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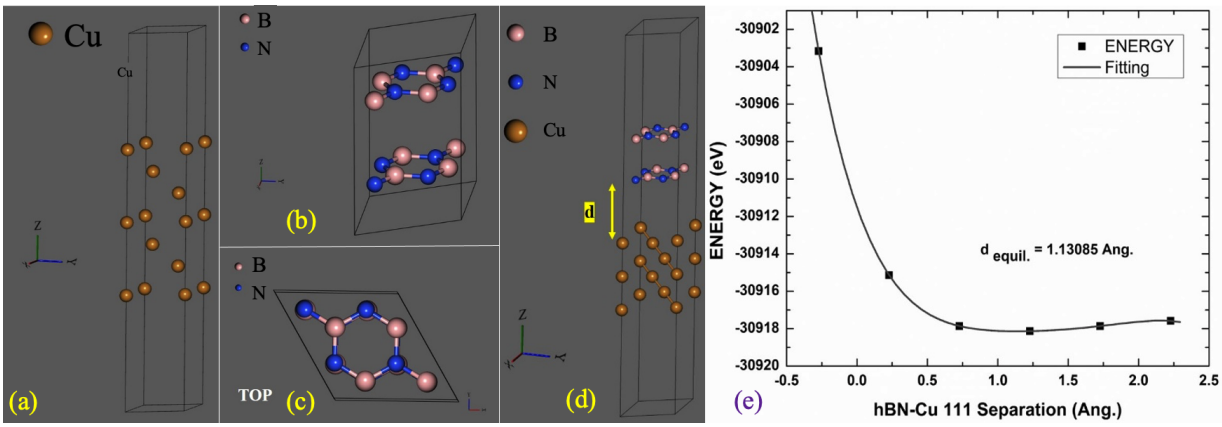

Figure 2: Illustrations of the atomic modeling of Cu (111) (a), hBN (b, c), and hBN/Cu (d, e) for the work function calculations in Quantum Espresso.

band-structure, etc. of thin-films. DFT was successfully used to calculate the work function (WF) of encapsulated alkali antimonides with 2D thin-films [6], where the authors used a commercial software VASP [8]. In our studies, we used an open-source software, Quantum Espresso, which is compatible with parallel computing on the NERSC supercomputer [9].

The WF of a material is the minimum energy required for electrons to escape the surface. We modelled encapsulation layers of hBN with Cu (111), Cs_3Sb, and K_2CsSb to calculate the effect of having the encapsulation layers on them. For the relevance of this paper, we only present the WF calculations with a Cu (111) substrate. The atomic models of the bulk and slab structures of Cu (111), hBN, and hBN encapsulated Cu (111) are shown in Fig. 2(a)-(d). The separation distance of the hBN layer from Cu was found via varying the distance and finding the minimum energy, as shown in Fig. 2(e). The WF of the Cu (111) decreases significantly by approximately 1.3 eV when encapsulated by two hBN monolayers. Our result yields work function values of 4.84 eV for the naked Cu (111), which agrees with the published data, and 3.53 eV for the hBN-encapsulated one. The average electrostatic potential and Fermi level for a naked Cu (111) substrate and a Cu (111) encapsulated with two monolayers of hBN are shown in Figs. 3(a) and 3(b), respectively.

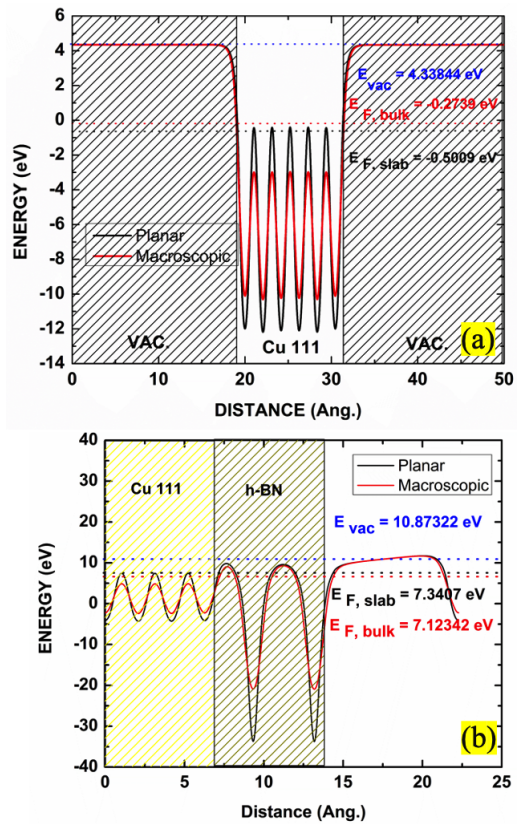

Figure 3: Work function calculation for (a): a naked Cu (111) substrate and (b): a Cu (111) substrate encapsulated with two monolayers of hBN.

QE MEASUREMENT RESULTS

To compare the DFT simulation results with experiments before we try the HPP reactive RF sputtering, we prepared samples of several kinds. We acquired dry N_2-sealed Cu substrates with both polycrystalline and single crystal (111) structures. For each kind of substrate, we wet transferred a monolayer of hBN on them and also did a "mock transfer" where the substrate went through the whole wet transfer process, including the post-processing heat treatment, only without the hBN thin-film. The mock transferred substrates had the same amount of exposure to water and air before they had the hBN monolayer transferred on them.

The QE measurements were done with a dedicated cathode testing system at Argonne National Laboratory's Argonne Wakefield Accelerator (AWA) facility. The light source was from a mercury lamp with a 254 nm bandpass filter with a full width half maximum (FWHM) spectrum of 10 nm. The photon flux was measured using a photon counter inside the chamber for the absolute QE calculation. The photocurrent measurements were done with a Keithley

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6487 picoammeter. The comparisons of measured QE for the aforementioned samples are shown in Fig. 4.

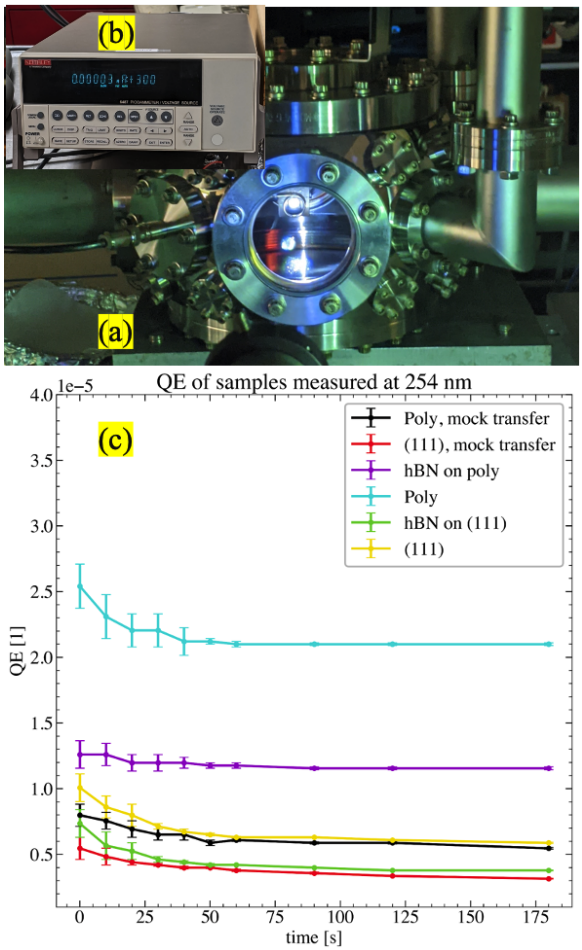

Figure 4: (a) and (b): The QE measurement system at AWA; (c): Measured QE of 6 different kinds of Cu substrates.

As can be seen, although the encapsulated substrates of both polycrystalline and single crystal (111) Cu showed lower QE compared to the fresh naked substrates, which was likely due to the oxidation during the wet transfer process, the encapsulated substrates exhibited higher QE compared to those prepared with the mock transfer process. This indicates that the hBN monolayer protected the substrates from further oxidation after the transfer was completed, and laid the foundation for our exploration of depositing hBN thin-films with the HPP reactive sputtering method.

HPP REACTIVE RF SPUTTERING OF BN THIN-FILMS

We used a dedicated sputtering system named "Turmeric", which is equipped with a RF magnetron and 600 Watt RF power source that supports a pulsed operation mode. All vacuum components used in the system are compatible with UHV and the system has a SAES NEG pump with which the ultimate base pressure can be as low as low 10^{-10} Torr. The chamber is connected with two mass flow controller (MFC)-controlled gas supply lines, one for ultrahigh purity (UHP) N_2 and the other for UHP Ar. A pyrolytic boron nitride (PBN) target was used and the distance between the target and substrate was maximized with a magnetically coupled actuator to avoid significant temperature rise (more than 100°). The setup is shown in Fig. 5(a), the XPS scan are shown in Fig. 5(b) and 5(c), and the Raman spectroscopy result is shown in Fig. 5(d). The strong B 1*s* and N 1*s* peaks in the spectrum and the similar intensity indicate the N_2 compensated the lost N after the original B-N bonds broke. The Raman shift data shows an extremely promising peak at approximately 1350 cm^{-1}, very close to the reported values of 1366 cm^{-1} in the literature for hBN and far away from the cBN peak at 1305 cm^{-1} [10] This suggests that the main component of the BN thin-film is in the hBN form.

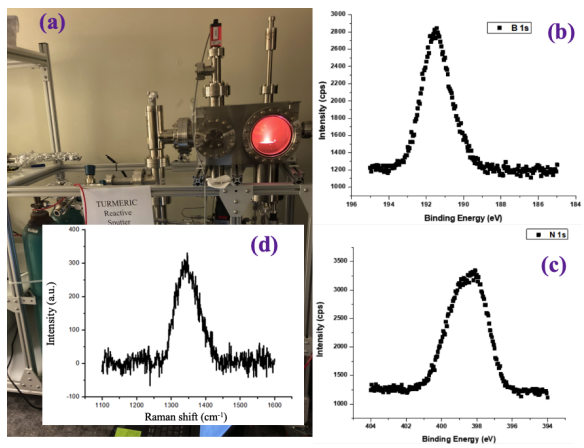

Figure 5: (a): The Turmeric HPP pulsed RF sputtering system; (b) and (c): XPS scan of the sputtered BN thin-film; (d): Raman spectroscopy of the thin-film.

CONCLUSION AND FUTURE WORK

We demonstrated the benefits and feasibility of directly depositing a thin film of hBN on photocathodes as an encapsulation mechanism. We showed the WF of a Cu (111) substrate could be reduced by the hBN thin-film and showed the Cu substrate can be protected by the encapsulation in a wet transfer procedure. The reason why the QE of the encapsulated substrate was lower than a naked one needs to be further studied to eliminate the oxidation effect during the transfer. We showed the HPP reactive RF sputtering was able to generate BN films of a hexagonal form. Further characterizations are needed to confirm the encapsulation and effects on the QE.

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