

DEPENDENCE OF CsK₂Sb PHOTOCATHODE PERFORMANCE ON THE QUALITY OF GRAPHENE SUBSTRATE FILM

L.Guo^{1,†}, K. Goto¹, H. Yamaguchi², M. Yamamoto³ and Y. Takashima¹

¹ Nagoya University, Nagoya, Aichi, Japan

² Los Alamos National Laboratory, Los Alamos, New Mexico, U.S.A.

³ High Energy Accelerator Research Organization, Tsukuba, Ibaraki, Japan

Abstract

A high-performance photocathode is required to advanced accelerators and electron microscopes. In particular, the CsK₂Sb photocathode is of interest because it has features such as low emittance, excitability with visible light, and high quantum efficiency (QE). Generally, the CsK₂Sb photocathode is produced by depositing a cathode element on a substrate, so that the cathode performance strongly depends on the surface condition of the substrate. We have found graphene as reusable substrate, which has the property of being chemically inactive. In this study, graphene film quality dependence of CsK₂Sb photocathode performance was evaluated. Specifically, CsK₂Sb photocathode was deposited using different quality graphene film substrates and their QE values and uniformity were compared. The quality of graphene films was analyzed using X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). We found that the graphene film can be cleaned by heating at 500 deg. The QE of the cathode on a good quality graphene film was higher and more uniform than that on a poor quality graphene film.

INTRODUCTION

Cesium potassium antimonide (CsK₂Sb) is one of the highest performing alkali (multi) antimonide photocathodes, achieving quantum efficiency that exceeds 10% by a green laser (532 nm)[1,2]. It is also realized of record-high beam current of 60 mA in a DC injector with 30 hours 1/e lifetime[3].

Generally, CsK₂Sb photocathode is produced by depositing the cathode element on a substrate, so that the cathode performance strongly depends on the substrate material, including crystallinity[1,4], surface state (contamination, roughness, and surface orientation)[1,4-6] and dopant types[2]. If the substrate after cathode production is used again by heat cleaning, the performance of the reproduced cathode will drastically deteriorate. Therefore, since the cathode performance is prioritized, the substrates are generally not reusable. On the other hand, the exchange of substrate takes an enormous amount of time and labor. This hinders basic research and practical application of photocathodes. As an effectual method to deal with this problem, we have coated graphene on the substrate as a protective layer.[7]

In this study, we investigated the QE and its mapping using different quality graphene film substrates to understand the effect of graphene film quality on the photocathode

[†] l.guo@nusr.nagoya-u.ac.jp

performance. For this purpose, we used XPS and XAS to evaluate the quality of graphene films. The CsK₂Sb photocathode was fabricated onto them, and their performance was compared.

EVALUATION OF GRAPHENE QUALITY

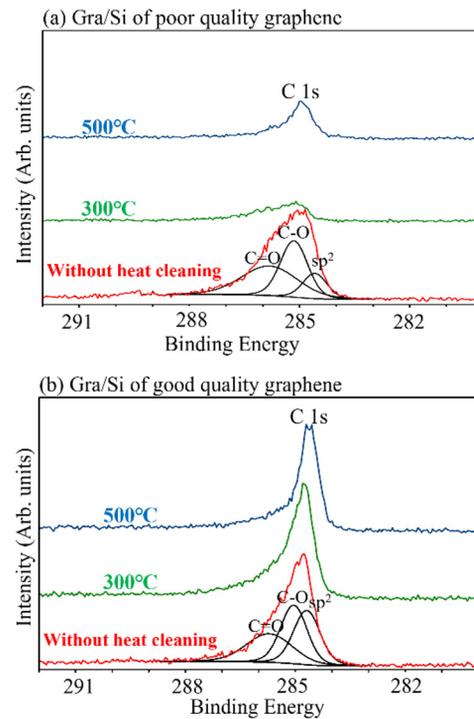


Figure 1: The XPS results of C 1s peaks for under different heat cleaning conditions. Red, green, and blue lines are for cleaning condition of without heat cleaning, 300°C, and 500°C, respectively. (a) is Gra/Si of poor quality graphene. (b) is Gra/Si of good quality graphene. The fitting for the sp², C-O, and C=O peaks are shown in the black lines below in the spectrum.

Graphene is produced on a Cu substrate by the chemical vapor deposition (CVD) method and transferred to Si substrate by a polymer support[8]. However, the Polymethyl methacrylate (PMMA) support remains on the graphene surface after transfer and must be removed. Considering the photocathode formation environment, the heat cleaning method under ultrahigh vacuum is used for the graphene-coated substrate.

We prepared two kinds of samples of graphene-coated Si substrate (Gra/Si), which one is Si coated with good quality graphene film, the other is Si coated with poor quality graphene film. They were analyzed of XPS and XAS under

© 2022, published by the International Particle Accelerator Conference (IPAC) under the Creative Commons Attribution License (CC BY 4.0). Any distribution of this work must maintain attribution to the author(s), title of the work, publisher, and DOI.

different heat cleaning condition. Measurements were performed at beamline (BL7U) of Aichi Synchrotron Radiation Center, Japan.

Figure 1 shows the XPS results of C 1s peaks for graphene of two samples under different heat cleaning conditions ($h\nu = 650$ eV). The information depth of the analyzed region is about 0.5–1 nm, which is determined by the electron inelastic mean-free path length and the take-off emission angle of 45° . The spectra were fit by the Doniach–Sunjic function after subtracting a Shirley background. We used CasaXPS software for the analysis after converting the kinetic energy of data to binding energy. Table I summarizes the composition percentage of sp^2 , C-O and C=O for the two samples under heat cleaning condition of without heat cleaning, 300°C , and 500°C . It is clear from figure 1 that the C 1s spectrum contains three peaks at about 284.6, 285.1, and 286.0 eV, corresponding to the sp^2 , C-O, and C=O, respectively. For the two samples, C 1s peak without heat cleaning has a wide peak width due to the three components of sp^2 , C-O and C=O, and it became sharp with heat cleaning. It shows that the PMMA support was removed by heating and the graphene film was observed.

C 1s peak for Gra/Si of poor quality graphene became weak after PMMA removal by heat cleaning (Figure 1a). The structure of graphene was found to be few. On the other hand, C 1s peak for Gra/Si of good quality became sharp as in the previous study[8] after PMMA removal by heat cleaning (Figure 1b). It is clear that quite a good quality of graphene was prepared. The XPS spectrum of graphene did not contain any elements other than C and O, indicating the absence of impurities.

Table 1: The composition % of sp^2 , C-O and C=O for heat cleaning condition of without heat cleaning, 300°C , and 500°C , respectively

Gra/Si of poor quality graphene	
Cleaning condition	sp^2 , C-O, C=O (%)
Without heat cleaning	11, 67, 22
300°C	30, 52, 18
500°C	43, 45, 12
Gra/Si of good quality graphene	
Cleaning condition	sp^2 , C-O, C=O (%)
Without heat cleaning	18, 45, 37
300°C	66, 18, 16
500°C	88, 7, 5

We then performed XAS to confirm the quality of graphene. Figure 2 shows the XAS results of the C K-edge under different heat cleaning conditions for the Gra/Si of two types of quality graphene film. π at 285eV and σ at 292eV. The σ and π band carbon structures for Gra/Si of poor quality graphene was weak after 500°C heat cleaning (Figure 2a). On the other hand, a strong σ and π band

carbon structures for Gra/Si of good quality graphene after 500°C heat cleaning is shown in Figure 2b. Since the shapes after 500°C and 600°C heat cleaning is almost the same, they show sufficient degeneracy at 500°C . It is shown that heating above 500°C was required to obtain a clean graphene surface. From these results, the quality of the graphene film could be confirmed.

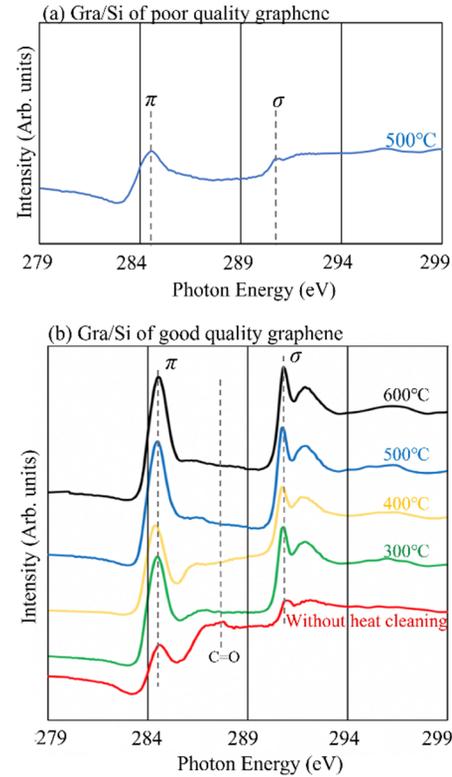


Figure 2: The XAS results of the C K-edge for the Gra/Si substrates of two types of quality graphene film under different heat cleaning conditions. Red, green, yellow, blue, and black lines indicate heat cleaning condition of without heat cleaning, 300°C , 400°C , 500°C , and 600°C , respectively.

QE MEASUREMENT

After confirming the quality of graphene by XPS and XAS, we deposited CsK₂Sb photocathode using the Gra/Si substrates of two types of quality graphene film. The experimental setup and cathode deposition techniques were described in Ref. [1, 2, 7]. Figure 3 shows that spectral response for a CsK₂Sb photocathode as a function of the photon energy on two kinds of these substrates. The laser spot size is about $\phi 0.4$ mm and the cathode was biased at -100 V. The typical photocurrent was $25 \mu\text{A}$. The photocurrent can be detected with a resolution of 0.1 nA. The error was calculated as the standard deviation for the eight measurements. The QE on Gra/Si of good quality graphene showed a satisfactory QE as high as 20% at 400 nm with a relatively small error bar, and it on Gra/Si of poor quality graphene was low 6% at 400 nm with a significant increase in the error bar.

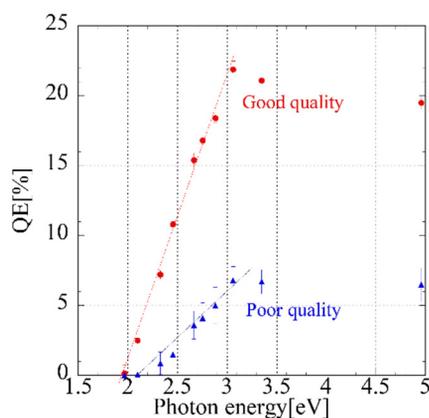


Figure 3: The Spectral response for a CsK₂Sb photocathode on different quality graphene film substrates. Red circles, and blue triangles are for the good quality graphene and poor quality graphene substrates, respectively. The red and blue dotted lines show the fitting results in the straight line from 2.0e V to 3.0eV.

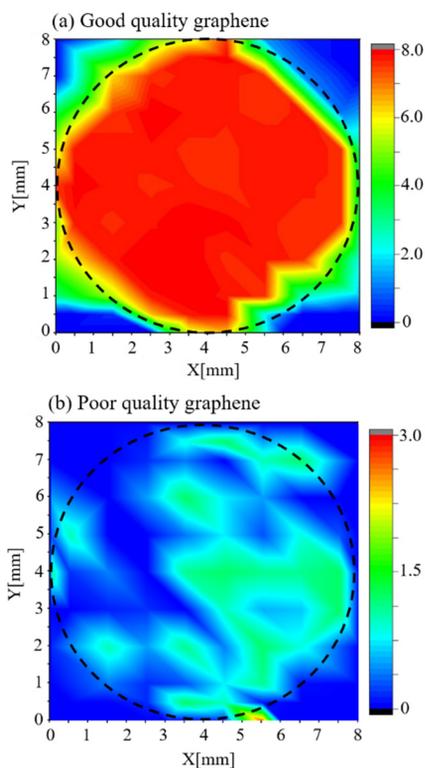


Figure 4: The QE mapping for a CsK₂Sb photocathode on different quality graphene film substrates. (a) The QE on good quality graphene substrate. (b) The QE on poor quality graphene substrate. The black dotted circle indicates the evaporation region of the CsK₂Sb.

The straight-line part from 2.0eV to 3.0eV can be fitted in a linear relationship, and X with $Y = 0$ is used as a work function. The work function on Gra/Si of poor quality graphene was about 2.1eV, not at 1.9eV of the CsK₂Sb photocathode. It suggests that the cathode is not properly formed. On the other hand, the result on Gra/Si of good quality graphene is consistent with a typical spectral response of CsK₂Sb photocathode [2,5-7]. The photocathode

performance of the Gra/Si of good quality graphene was higher than that of Gra/Si of poor quality graphene. This is the experimental evidence that the CsK₂Sb photocathode performance depends on the quality of graphene.

We also used 532nm laser ($h\nu = 2.33$ eV) to measure QE mapping on the two kinds of Gra/Si substrates in Figure 4. The value on the X and Y axis is the movement amount of the XY-stage used for measurement. Figure 4a shows a high and uniformly QE of the Gra/Si substrate of good quality graphene. The dispersion of QE within the deposition range is 5% or less. On the other hand, a low and island-shaped QE on the Gra/Si substrate of poor quality graphene is shown in Figure 4b. It is shown that the quality of graphene affects not only the maximum of QE but also the uniformity of QE.

The reason for the low photocathode performance on poor quality graphene is that amorphous carbon contaminates the substrate surface and interferes with the formation of the photocathode.

SUMMARY

We studied the graphene quality dependence of CsK₂Sb photocathode performance. We used two kinds of Gra/Si substrates, one is Si coated with good quality graphene film, the other is Si coated with poor quality graphene film and evaluated the qualities of graphene by XPS and XAS. We found that heating above 500°C was required to obtain a clean graphene surface. We fabricated CsK₂Sb cathodes on them and compared their performance. We found that the cathodes on good quality graphene had significantly better performance than on poor quality graphene. This showed that the cathode performance depends strongly on the quality of graphene.

ACKNOWLEDGEMENTS

The authors would like to thank researchers Nakatake and Takakura of Aichi Synchrotron Radiation Center BL7U for their support of XPS and XAS measurement.

The work was financially supported by the High Energy Accelerator Research Organization (KEK), Japan for the Japanese team and the U.S. Department of Energy (DOE) Office of Science for the U.S. team under the U.S.-Japan Science and Technology Cooperation Program in High Energy Physics.

REFERENCES

- [1] L. Guo *et al.*, "Substrate dependence of CsK₂Sb photocathode performance", *Prog. Theor. Exp. Phys.*, vol. 2017, p. 033G01, 2017. doi:10.1093/ptep/ptx030
- [2] L. Guo and M. Katoh, "pn-type substrate dependence of CsK₂Sb photocathode performance", *Phys. Rev. Accel. Beams*, vol. 22, p. 033401, 2019. doi:10.1103/PhysRevAccelBeams.22.033401
- [3] B. Dunham *et al.*, "Record high-average current from a high-brightness photoinjector", *Appl. Phys. Lett.*, vol. 102, p. 034105, 2013. doi:10.1063/1.4789395
- [4] A. H. Sommer, *Photoemissive Materials*, Krieger, New York, 1968. doi:10.1016/S0079-1970(13)70009-4
- [5] H. Yamaguchi *et al.*, "Quantum Efficiency Enhancement of Bialkali Photocathodes by an Atomically Thin Layer on Substrates", *Phys. Status Solidi A*, vol. 216, p. 1900501 2019. doi:10.1002/pssa.201900501
- [6] H. Yamaguchi *et al.*, "Free-Standing Bialkali Photocathodes Using Atomically Thin Substrates", *Adv. Mater. Interfaces*, vol. 5, p1800249, 2018. doi:10.1002/admi.201800249
- [7] L. Guo *et al.*, "Graphene as reusable substrate for bialkali photocathodes", *Appl. Phys. Lett.*, vol. 116, p. 251903, 2020. doi:10.1063/5.0010816
- [8] A. Reina *et al.*, "Transferring and Identification of Single- and Few-Layer Graphene on Arbitrary Substrates", *J. Phys. Chem. C*, vol. 112, p. 46, 2008. doi:10.1021/jp087380s