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PHOTON-ENHANCED THERMIONIC EMISSION IN CESIATED P-TYPE AND N-TYPE SILICON

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ABSTRACT: Photon-enhanced thermionic emission (PETE) is a relatively new concept for high efficiency solar cells that utilize not only the energy of electrons excited across the band gap by photons, as in conventional photovoltaic solar cells, but also the energy usual lost to thermalization of the excited electrons. Efficiencies above 60% have been predicted theoretically for high solar concentration systems. Silicon is an interesting absorber material for high efficiency PETE solar cells, partly due to its mechanical and thermal properties and partly due to its electrical properties, including a close to ideal band gap. The work function of silicon is, however, too high for practical PETE implementations. A well-known method for lowering the work function of silicon (and other materials) is to apply approximately a monolayer of cesium to the silicon surface. We present the first measurements of PETE in cesiated p-type and n-type silicon. It is shown that PETE in average can increase the thermionic emission current by more than an order of magnitude.

Keywords: Silicon, Solar Cell Efficiencies, Characterization

1 INTRODUCTION

In the search for high efficiency solar cells, several new designs have been suggested in recent years. Among these, solar cells based on photon-enhanced thermionic emission (PETE) have recently received great interest due to the promise of technical efficiencies of up to or exceeding 60% [1,2]. The PETE cell consists of an illuminated semiconductor cathode and a metal anode and possibly a thermal engine producing electrical energy from the thermal energy of the anode. The high efficiency of PETE cells is obtained by thermionic emission of electrons from the cathode that carry energy from photon excitation as well as thermal energy in the system. Thus high efficiency PETE cells rely on high solar concentration and high cell temperature. However, recent detailed balance calculations show that efficiency could be drastically reduced due to especially surface and Auger recombination [3,4].

The PETE effect has so far been demonstrated experimentally in GaN and a GaAs/AlGaAs heterostructure with a quantum efficiency of 0.14% (at 330 nm) and 1.4% (at 850 nm), respectively [5]. Silicon is widely used for solar cells partly due to its relatively low cost and widespread use in semiconductor industry and partly due to suitable mechanical, electrical and optical properties. For PETE solar cells a low work function is, however, also necessary. The work function of silicon can be lowered by cesium coating of the silicon surface.

In this paper we present results on PETE in highly doped cesiated n-type and p-type silicon. Using a UHV chamber with a 940 nm laser source, X-ray Photoelectron Spectroscopy (XPS) system and cesium evaporation source we measure the thermionic current for both sample types in the dark and during illumination (figure 2). The photon-enhancement due to illumination is found to be largest in p-type silicon as predicted by theoretical models, with a relative increase in thermionic current during illumination that is up to 1.6 times that of n-type silicon. In the temperature interval 400 K to 600 K, the average relative increase in thermionic current due to illumination is 10.8 for n-type cesiated silicon and 17.4 for p-type cesiated silicon (figure 3).

2 THEORY

The ideal thermionic current density, J, from a PETE solar cell is given by a slightly modified Richardson-Dushman equation

$$J = A^* T_c{}^2 \exp\left(-\frac{\varphi - (E_{f,n} - E_f)}{k_B T_c}\right)$$

where A^* is the Richardson constant, T_c is the cathode temperature, φ is the work function, $E_{f,n}$ is the electron quasi Fermi level, E_f is the Fermi level and k_B is Boltzmann's constant. The PETE effect is simply the reduction of effective work function due to quasi-Fermi level splitting.

In non-ideal thermionic devices the electrons in transit in the gap between the cathode and anode will create an additional space-charge potential barrier in the gap for electrons to overcome in order to reach the anode. The space-charge potential barrier effectively reduces the thermionic current. In this space-charge regime the current density is [6]

$$J = en_e \left(\frac{2k_B T_c}{\pi m_e}\right)^{\frac{1}{2}} \exp \gamma,$$

where e is the electron charge, n_e is the maximum electron density in the gap, m_e is the electron mass and $\gamma = -(\varphi_m - \varphi)/(k_B T_c)$ with φ_m being the space-charge barrier energy. Thermionic systems with a large gap between the cathode and the anode and without any space-charge compensation will operate in the space-charge regime.

While silicon in general is a very interesting material for solar cells, the main disadvantage when using silicon in a PETE solar cell is its high work function of approximately 4.5 eV which drastically reduces the thermionic emission current.

A commonly used approach to reduce the barrier experienced by electrons at the silicon surface is to apply a cesium or cesium oxide coating approximately 1 monolayer thick, thereby reducing the work function by several eV. Unfortunately, such cesium coatings are only stable at temperatures below approximately 550 K [7], where the thermionic current is typically very small.

However, for an actual PETE solar cell device one could have a cesium gas in the gap between the cathode and anode. This would allow for operation at higher temperatures since the cesium background pressure would reduce evaporation and also have a space-charge reducing effect due to the presence of positive ions. Also, as will be shown in the following, a measureable thermionic current can be generated even at temperatures below 550K due to PETE thus reducing the need for high temperature operation.

3 EXPERIMENTS

The experimental setup, shown in figure 1, consists of a UHV chamber fitted with a XPS system, a cesium evaporator, a 2 W laser source (operating at 940 nm) for sample illumination, a sample holder with built-in thermocouple in contact with the silicon sample and a Cu plate anode for collecting the thermionic current. The anode is located approximately 1 mm from the silicon cathode. The sample holder also contains a resistive heating filament for heating the silicon sample from the backside. Electrical contact to the sample is obtained through molybdenum clips which also fixate the sample. The samples are illuminated from the front side (i.e. the electron emitting side). Two 1.5 cm × 1.5 cm silicon samples were prepared; a boron doped p-type sample and an antimony doped n-type sample. Both samples had electrical resistivities of less than 0.025 Ω·cm. Since the difference between the electron quasi Fermi level and the Fermi level is smaller in illuminated highly doped n-type silicon than in illuminated highly doped p-type silicon, it is expected that the PETE effect is less pronounced in the n-type sample than in the p-type sample. In order to make sure that thermionically emitted electrons are collected at the anode and not at e.g. the sample holder, a positive bias voltage is applied to the anode.

5 EXPERIMENTAL RESULTS

The UHV chamber was pumped to a base pressure of 10^{-9} mbar and the initial work function of the silicon samples were found by XPS to 4.5 eV using a gold reference sample for calibration. A small amount of oxygen on the samples was also noticed in the XPS spectra and was attributed to native oxide on the silicon surfaces. Samples were cleaned in the chamber by argon ion sputtering. Cesium was evaporated onto the silicon surfaces thereby reducing the work functions by 2.1 eV according to XPS. Also, the cesium was stable over time, showing no increase in work function after several weeks. Repeated heating experiments showed that the cesium coating was indeed stable at temperatures up to 550 K. A slight increase in the work function was detected after heating the samples to 600 K, indicating evaporation of cesium from the samples. At sample temperatures close to room temperature the temperature increase due to illumination was 10 K for the p-type sample and 30 K for the n-type sample. At higher sample temperatures the temperature increase was smaller.

The thermionic current as function of temperature was measured with a bias voltage of 50 V in the dark and illuminated, see Figure 2. For this bias voltage and up to above 200V the thermionic emission was found to be in the space-charge regime as I-V characteristics followed

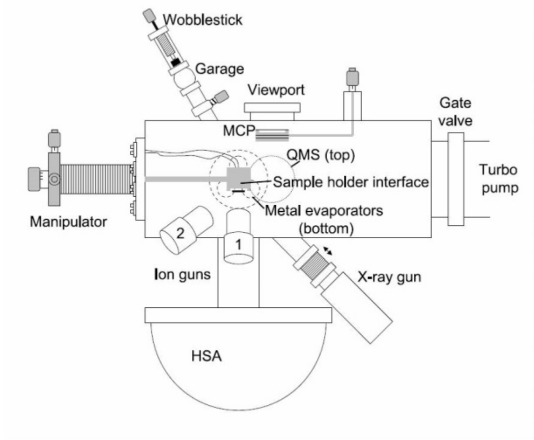

Figure 1: Top view of the UHV chamber used for cesium deposition and thermionic measurements. The PETE effect is investigated by illuminating the sample with a laser source through a laser feed-through in the chamber.

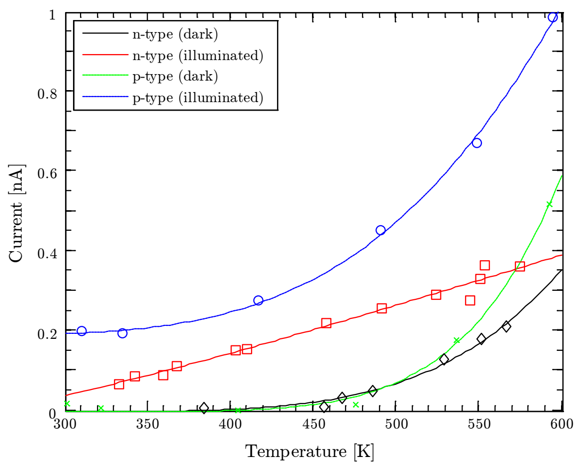

Figure 2: The measured thermionic current from cesiated n-type and p-type silicon at temperatures up to 600K. The current is for both samples increased by illumination. The curves are fits to data using the space-charge model Eqn. 2.

the Child-Langmuir law. Fits to the measured data using the space-charge model in Eqn. 2 resulted in a maximum root-mean-square error of 0.018. It is clearly seen that the thermionic current is increased by illumination. Since the increase occurs at low temperatures and with a photon energy well below the samples work functions these measurements are consistent with the predictions of the PETE model [1].

It is noted that the measured currents are in the order of nA. This relatively low current, and thus low technical efficiency, is contributed to several factors including large cathode to anode distance causing substantial space-charge and misalignment of the cathode and anode due to positioning for front side illumination. Also, a small but non-negligible reverse current is expected as the copper anode reaches a thermal equilibrium with the anode through radiative heat transfer and since it is expected that a certain amount of cesium is present on the anode surface. The relative increase in thermionic current due to illumination is shown in Figure 3 for both n-type and p-type silicon. In order to compensate for the difference in onset of measurable thermionic current in the two samples, a temperature scale normalized with respect to the temperature at which the current exceeds 1 pA is used. It is found that the relative current increase is largest for p-type silicon with an average increase of a factor of 17.4. For n-type silicon the average increase is by a factor 10.8. The effect of illumination is decreasing with temperature as conventional thermionic emission begins to dominate. Defining the two ratios

$$r = \frac{J_{\text{Illuminated,n}}}{J_{\text{Dark,n}}} \text{ and } r_p = \frac{J_{\text{Illuminated,p}}}{J_{\text{Dark,p}}}$$

for n-type and p-type samples, respectively, the ratio r_p/r is plotted in Figure 4. It is seen that the relative increase during illumination in the p-type silicon sample is between 1.25 and 1.67 times that of the n-type silicon sample, which further supports that the measured increase in current during illumination is due to PETE. At temperatures close to 600 K the model uncertainties increases as the data becomes increasingly affected by loss of cesium due to evaporation.

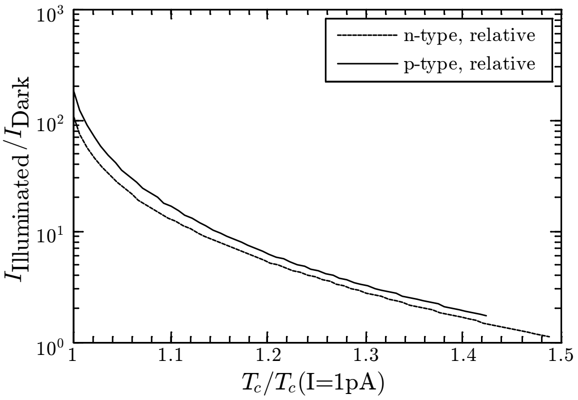

Figure 3: The relative increase in thermionic current due to illumination for cesiated n-type and p-type silicon samples. The temperature is normalized with respect to the temperature where the thermionic current is 1 pA.

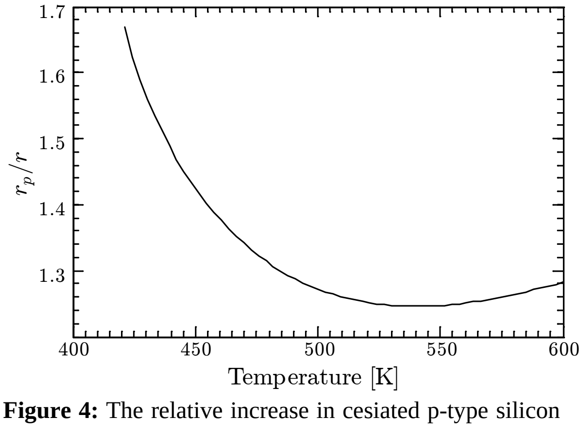

Figure 4: The relative increase in cesiated p-type silicon is up to 1.6 times larger than that of cesiated n-type silicon.

6 CONCLUSION

The effect of illumination on the thermionic emission from cesiated n-type and p-type silicon has been measured. A space-charge limited model was fitted to the measured data and it was found that illumination can increase the thermionic current at temperatures below the onset of dark thermionic emission by more than an order of magnitude and in average by a factor of 17.4 for p-type silicon and 10.8 for n-type silicon in the considered temperature interval. It was found that the relative increase in thermionic current due to illumination is up to 1.6 times larger in cesiated p-type silicon than in cesiated n-type silicon.

These results show that the photon-enhancement of the thermionic emission in cesiated silicon is indeed very large and that an efficient PETE solar cell based on a cesiated silicon cathode is realistic, especially if the space charge is limited by e.g. reducing cathode to anode distance.

6.1 Acknowledgements

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REFERENCES

[1] J. W. Schwede, I. Bargatin, D. C. Riley, B. E. Hardin, S. J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R. T. Howe, Z.-X. Shen, N. A. Melosh, *Nature Materials.* **2010**, 9.

[2] K. Reck, O. Hansen, *Applied Physics Letters*, **2014,** 104 (2), 023902

[3] G. Segev, Y. Rosenwaks, A. Kribus, *Solar Energy Materials & Solar Cells*, **2012**, 107.

[4] A. Varpula, M. Prunnila, *Journal of Applied Physics*, **2012**, 112, 044506

[5] J.W. Schwede, T. Sarmiento, V.K. Narasimhan, S.J. Rosenthal, D.C. Riley, F. Schmitt, I. Bargatin, K. Sahasrabuddhe, R.T. Howe, J.S. Harris, N.A. Melosh & Z.-X. Shen, *Nature Communications.* **2013**, *4*.

[6] G. N. Hatsopoulos, E. P. Gyftopoulos, *Thermionic Energy Conversion*, MIT Press, **1979**

[7] D. Edwards, W. T. Peria, *Applications of Surface Science.* **1978**, 1, 4.