Germanium Photovoltaic Cells with MoO_x Hole-Selective Contacts

A. Alcañiz[(a)], G. López[(a)], I. Martín[(a)], A. Jiménez [(b)], A. Datas[(a,b)], E. Calle[(a)], E. Ros [(a)], L.G. Gerling[(a)], C. Voz[(a)], C. del Cañizo[(b)], R. Alcubilla[(a)]

[(a)] Electronic Engineering Department, Universitat Politècnica de Catalunya, Jordi Girona 1-3, Barcelona 08034, Spain

[(b)] Instituto de Energía Solar, Universidad Politécnica de Madrid, 28040 Madrid, Spain.

Keywords: germanium, MoOx, transition metal oxide, solar cell, thermophotovoltaics, photovoltaics.

Abstract

Very thin, thermally evaporated MoO_x (x<3) layer has been used as transparent hole-selective contact on an n-type Germanium substrate to effectively demonstrate PV conversion capability. The fabricated MoO_x/Ge heterojunction PV cell shows a photocurrent density of 44.8 mA/cm^2 under AM1.5G illumination, which is comparable to that of conventional Ge PV cells. However, a low open-circuit voltage of 138 mV is obtained, which might be explained by the presence of tunnelling mechanisms through the MoO_x/Ge interface. To our knowledge, this is the first demonstration of a hole-selective contact made of transition metal oxide on an n-type semiconductor different from c-Si. Thus, this work may have important implications toward the development of new device architectures, such as novel low-cost Ge PV cells with possible applications in multijunction solar cells and thermophotovoltaics.

Main text

Historically, the driving force for the use of Ge in photovoltaic (PV) applications has been as a substrate for GaAs space solar cells (Miller and Harris 1980), the main reason being the higher thermal conductivity and the possibility of manufacturing thinner and lighter wafers with Ge than with GaAs. Later on, Ge/GaAs tandem solar cells were pursued to enhance the conversion efficiency (Chand et al. 1986) by using the Ge bottom cell to convert the infrared part of the solar spectrum. This progress eventually derived in the development of the current standard technology for space solar cells that consists of triple junction Ge/GaAs/GaInP structures, with AM0 conversion efficiencies in the range of 28-30%. These cells have been also used in terrestrial applications within concentrated-PV (CPV) systems, where they reached AM1.5D conversion efficiencies of 41.6% (R.R. King et al. 2009), just slightly below the current worldrecord for solar-to-electricity conversion efficiency of 46.0% (Dimroth et al. 2014). Apart from solar applications, Ge PV cells have been considered as a low-cost replacement for low band gap III-V semiconductors in thermophotovoltaic (TPV) converters, in which thermal radiation is directly converted into electricity by infrared sensitive PV devices (Bauer 2011; Chubb 2007). In this context, Ge TPV cells could be used in a broad range of applications such as waste heat recovery (Bauer et al. 2003), solar-thermal power (Ungaro, Gray, and Gupta 2015; Lenert et al. 2014; Alejandro Datas and Algora 2013), space power (A. Datas and Martí 2017), and energy storage (Alejandro Datas et al. 2016), among many others.

Current state of the art of Ge PV cells consist of p-n junctions created by diffusion of dopants at high temperatures (Bitnar 2003). For instance, p-n junctions in p-Ge have been created by diffusion of V-group atoms (typically P and As) during the first growing step of GaInP or GaAs nucleation layers within a Metal-Organic CVD (MOCVD) reactor at temperatures of ~ 650ºC (Fernandez et al. 2008; Fernández 2010; Barrigón Montañés 2014). Other groups have used the diffusion of Zn in n-Ge substrates within a LPE reactor (Khvostikov et al. 2002). In an effort to reduce manufacturing costs of standalone Ge PV cells, IMEC reported devices with p-n junctions created by spin-on diffusion of P on p-Ge by rapid thermal annealing at different temperatures (450-700 °C) (Posthuma et al. 2007; van der Heide 2009; van der Heide et al. 2009) leading to the best reported 1-sun AM1.5G conversion efficiency for stand-alone Ge PV cells of 7.9% (van der Heide et al. 2009). Surface passivation has been accomplished by forming different kinds of heterojunctions on Ge surface, such as Ge/GaAs (Khvostikov et al. 2002) or Ge/GaInP (Fernandez et al. 2008; Fernández 2010; Barrigón Montañés 2014) by MOCVD or LPE (Khvostikov et al. 2002), or Ge/a-Si (Posthuma et al. 2007; van der Heide 2009; van der Heide et al. 2009; Posthuma et al. 2005), Ge/SiNx (Nagashima, Okumura, and Yamaguchi 2007) and Ge/a-Si_xC_{1-x} (Fernandez et al. 2008; Fernández 2010) by PECVD.

In order to further reduce the fabrication cost of Ge PV cells, it is desirable to eliminate the high temperature diffusion, and complex MOCVD or PECVD processes. In this regard, a particularly appealing option consists of substituting the doping step by carrier-selective coatings with surface passivation properties that could be deposited at low temperatures. For this purpose, high electron-affinity transition metal oxides (TMOs) such as MoO_3, WO_3, and V_2O_5, are very interesting candidates that have already been found effective to produce hole-selective contacts on both n-type and p-type c-Si (Gerling et al. 2016; Battaglia et al. 2014; Bullock et al. 2014).

In this letter we report a Ge PV cell formed by a thin sub-stoichiometric MoO_x ($x<3$) layer on top of an n-type crystalline Ge (c-Ge) substrate, which behaves as a hole selective contact. To our knowledge, this is the first demonstration of a hole-selective contact made with a TMO on an n-type semiconductor different than c-Si. Thus, it might open the door to new device architectures, not only for PV applications, but also in photonics and CMOS electronics, where the integration of TMOs is being investigated (Sanchez et al. 2016), along with the use of different semiconductors having higher carrier mobilities and extended spectral response than c-Si, such as Ge (Reboud et al. 2017; Toriumi and Nishimura 2017).

The PV cell structure was fabricated on (100) oriented, Czochralski, n-type Ge substrates (ρ= 0.37 Ω·cm, 350 µm-thick). The substrate was cleaned by HCl: H_2O (33%) immediately prior to rear side passivation by PECVD of (i/n$^+$) a-SiC_x:H (4/15nm, x~0.2) and a-SiC (80nm) stack deposited at ~ 300ºC. Next, the rear contact was created by laser firing of the a-SiC stack to produce an array of ~ 60 µm diameter local diffusion points, separated by 600 µm pitch. Laser firing was accomplished by means of a ~1200 mW, λ= 1064 nm Nd/YAG laser system at a frequency of 4 kHz with 6 pulses per spot, following a similar approach than in (López et al. 2018) . The rear contact was finalized by means of an e-beam evaporated Ti/Pd/Ag metal stack that provides lateral interconnection between fired points. The hole selective contact was formed at the front side of the device by means of very thin (nominally 20 nm) MoO_x layer thermally evaporated from powdered MoO_3 sources at ~$8\cdot10^{-6}$ mbar and a deposition rate of ~ 0.2 Å/s. A 75 nm-thick ITO layer was subsequently deposited by RF-Sputtering on top of the MoO_x layer to increase lateral electrical conductivity and minimize optical reflectivity. A sketch of the full PV cell structure and the TEM image of the MoOx/ITO interface are shown in Figure 1, where a pronounced inter-diffusivity between the layers is clearly observed. The 1x1 cm^2 active area of the PV cells was defined by conventional lithographic techniques followed by mesa etching of the MoO_x/ITO layers. Finally, the front Ag grid electrode (2 µm thick) was evaporated through a shadow mask for a 4% contacted area

The current density-voltage (*J*-*V*) curve under 1-sun illumination is shown in Figure 2. The short-circuit current density (J_{SC}= 44.8 mA/cm^2) outperforms that of the best performing state of the art Ge PV cells (43.2 mA/cm^2) (van der Heide et al. 2009). On the other hand, a much lower open circuit voltage (138 mV) is measured, compared to those reported in (Fernández 2010; van der Heide et al. 2009) (up to 265 mV), which ultimately results in a lower FF (40.9 %), partially due to a non-optimized metal grid that introduces a series resistance of 0.65 Ωcm^2. As a result, an AM1.5G conversion efficiency of 2.53 % is obtained.

External quantum efficiency (EQE) of the PV cell is shown in Figure 3 at short-circuit conditions along with the EQE of Ge PV cells reported in (van der Heide 2009) for a direct comparison. The improved EQE for wavelengths shorter than 600 nm might be explained by the reduction of the recombination close to the front surface compared to the one existing in the highly-doped emitters (10^{19}-10^{21} cm^{-3}) used in (van der Heide 2009). Such a low recombination does not necessary indicate a good chemical surface passivation, i.e. strong reduction of interface state density, but it could be related to a strong electric field that unbalances carrier densities, i.e. field-effect passivation. In order to measure the electrostatic potential barrier built at the junction (V_{bi}), capacitance-voltage measurements in reverse bias were performed following the same approach than in (Almora et al. 2017) where similar structures on c-Si substrates are characterized. This data can be obtained by fitting the C^{-2} vs. V curve, known as Mott-Schottky plot, using the following equation $1/C^2 = 2(V_{bi} - V - 2k_BT/q)/q\varepsilon_S N_D$, where symbols have their usual meanings. By applying this model to the experimental data, we get an almost perfect linear fit (R^2=0.99988) leading to V_{bi} =317±4 mV. Additionally, the doping density (N_D) can be obtained from the slope of the curves leading to a N_D value of $6.9\pm0.1\cdot10^{15}$ cm^{-3}, which fully agrees with the Ge substrate specifications. The calculated V_{bi} indicates that the surface is highly inverted, i.e. hole density at the surface is even higher than the doping density $N_{D,}$ reducing interface recombination due to the scarce availability of electrons. This might explain the relatively high EQE values measured under short-circuit conditions in the UV-visible range.

In order to investigate the origin of the low V_{OC}, a further understanding of the current mechanisms taking place in the MoO_x/Ge heterojunction is needed. With this aim, open-circuit voltage (V_{OC}) is measured as a function of photogenerated current (J_{ph}) by means of a flash lamp. For every flash, V_{oc} values of the cell are recorded in an oscilloscope, while J_{ph} is estimated from the light intensity measured by a reference Ge PV cell (Kerr, Cuevas, and Sinton 2001). It is well known that applying the superposition principle and taking into account that the device is kept under open-circuit conditions, J_{ph} must be equal to the current that would be measured in the cell at dark conditions and the series resistance has no effect on the measurement. As a consequence, the analysis of J_{ph}-V_{OC} curves enables the extraction of useful information otherwise hidden by the series resistance effects in conventional dark *J*-*V* characteristics. This advantage is crucial in our devices given the combination of relatively high currents with significant series resistance. Figure 4 shows the J_{ph}-V_{oc} curves measured at temperatures ranging 293-323 K in 5 K steps. The experimental data are fitted to an exponential trend given by $J_{ph} = J_0(T)[\exp(A(T)\cdot V_{OC}) - 1]$ and two examples for the highest and lowest temperature measurement are also shown in Figure 4. Notice that in this model no series resistance is included and consequently we have only two free parameters: the saturation current density, J_0(T), and the exponential factor, *A(T)*. In Figure 5 we show the Arrhenius plot of these parameters where a constant value of $A \approx 34$ V^{-1} and an activation energy of 0.462 eV for $J_0(T)$ suggests that tunnelling mechanism dominates at the MoO_x/Ge interface (Sze and Ng, n.d.). This tunnelling current jeopardizes the electron blocking properties of the junction leading to a high saturation current density and, thus, low V_{oc} values. A deeper knowledge of the band structure and interface characteristics of MoO_x/Ge junction is needed to fully understand how this tunnel mechanism takes place and to improve the obtained V_{oc} values.

In conclusion, we have reported for the first time a heterojunction MoO_x/Ge PV cell that effectively demonstrates the possibility of creating hole selective contacts in n-type c-Ge. Photovoltaic performance of the device shows excellent J_{sc} values (44.8 mA/cm^2) mainly related to an enhanced spectral response at short wavelengths. On the other hand, low V_{oc} values (138 mV) might be explained by an excess of tunnel current at the MoO_x/Ge interface resulting in high saturation currents. With evident room for improvement, these results could eventually open a new route for cost-reduction of Ge-based PV devices, including the development of new kind of low cost thermophotovoltaic converters. Eventually, it could also open the door for the integration of transition metal oxides in Ge photonics and CMOS electronics.

Acknowledgements

This work was supported by MINECO (Ministerio de Economía y Competitividad de España) under Thin-IBC [TEC2017-82305-R], CHENOC [ENE2016-78933-C4-1-R], and TORMES [ENE2015-72843-EXP] projects, and by the EU project AMADEUS, which has received funds from the Horizon 2020 research and innovation program, FET-OPEN action, under grant agreement no. 737054. A.Datas acknowledges postdoctoral fellowship support from the Spanish "Juan de la Cierva-Incorporación" program (IJCI-2015-23747). The sole responsibility for the content of this publication lies with the authors. It does not necessarily reflect the opinion of the European Union. Neither the REA nor the European Commission are responsible for any use that may be made of the information contained therein.

References

Almora, Osbel, Luis G. Gerling, Cristóbal Voz, Ramón Alcubilla, Joaquim Puigdollers, and Germà Garcia-Belmonte. 2017. “Superior Performance of V2O5 as Hole Selective Contact over Other Transition Metal Oxides in Silicon Heterojunction Solar Cells.” *Solar Energy Materials and Solar Cells* 168 (August): 221–26. https://doi.org/10.1016/j.solmat.2017.04.042.

Barrigón Montañés, Enrique. 2014. “Development of GaInP/GaInAs/Ge TRIPLE-Junction Solar Cells for CPV Applications.” Phd, E.T.S.I. Telecomunicación (UPM). http://oa.upm.es/30449/.

Battaglia, Corsin, Xingtian Yin, Maxwell Zheng, Ian D. Sharp, Teresa Chen, Stephen McDonnell, Angelica Azcatl, et al. 2014. “Hole Selective MoOx Contact for Silicon Solar Cells.” *Nano Letters* 14 (2): 967–71. https://doi.org/10.1021/nl404389u.

Bauer, T. 2011. *Thermophotovoltaics: Basic Principles and Critical Aspects of System Design*. Green Energy and Technology. Springer.

Bauer, T., I. Forbes, R. Penlington, and N. Pearsall. 2003. “The Potential of Thermophotovoltaic Heat Recovery for the Glass Industry.” In , edited by J. Coutts Timothy, Guazzoni Guido, and Luther Joachim, 653:101–10. AIP.

Bitnar, Bernd. 2003. “Silicon, Germanium and Silicon/Germanium Photocells for Thermophotovoltaics Applications.” *Semiconductor Science and Technology* 18 (5): S221. https://doi.org/10.1088/0268-1242/18/5/312.

Bullock, James, Andres Cuevas, Thomas Allen, and Corsin Battaglia. 2014. “Molybdenum Oxide MoOx: A Versatile Hole Contact for Silicon Solar Cells.” *Applied Physics Letters* 105 (23): 232109. https://doi.org/10.1063/1.4903467.

Chand, N., J. Klem, T. Henderson, and H. Morkoç. 1986. “Diffusion of As and Ge during Growth of GaAs on Ge Substrate by Molecular-beam Epitaxy: Its Effect on the Device Electrical Characteristics.” *Journal of Applied Physics* 59 (10): 3601–4. https://doi.org/10.1063/1.336790.

Chubb, D. L. 2007. *Fundamentals of Thermophotovoltaic Energy Conversion*. Elsevier.

Datas, A., and A. Martí. 2017. “Thermophotovoltaic Energy in Space Applications: Review and Future Potential.” *Solar Energy Materials and Solar Cells* 161 (March): 285–96. https://doi.org/10.1016/j.solmat.2016.12.007.

Datas, Alejandro, and Carlos Algora. 2013. “Development and Experimental Evaluation of a Complete Solar Thermophotovoltaic System.” *Progress in Photovoltaics: Research and Applications* 21 (5): 1025–39. https://doi.org/10.1002/pip.2201.

Datas, Alejandro, Alba Ramos, Antonio Martí, Carlos del Cañizo, and Antonio Luque. 2016. “Ultra High Temperature Latent Heat Energy Storage and Thermophotovoltaic Energy Conversion.” *Energy* 107 (July): 542–49. https://doi.org/10.1016/j.energy.2016.04.048.

Dimroth, F., M. Grave, P. Beutel, and C. Fiedeler. 2014. “Wafer Bonded Four-Junction GaInP / GaAs // GaInAsP / GaInAs Concentrator Solar Cells with 44.7% Efficiency.” *Prog. Photovolt: Res. Appl* 22: 277–82.

Fernández, J. 2010. “Optimization of Crystalline Germanium for Thermophotovoltaic and High-Efficiency Solar Cells.” University Konstanz.

Fernandez, J., S. Janz, D. Suwito, E. Oliva, and F. Dimroth. 2008. “Advanced Concepts for High-Efficiency Germanium Photovoltaic Cells.” In *2008 33rd IEEE Photovoltaic Specialists Conference*, 1–4. https://doi.org/10.1109/PVSC.2008.4922631.

Gerling, Luis G., Somnath Mahato, Anna Morales-Vilches, Gerard Masmitja, Pablo Ortega, Cristobal Voz, Ramon Alcubilla, and Joaquim Puigdollers. 2016. “Transition Metal Oxides as Hole-Selective Contacts in Silicon Heterojunctions Solar Cells.” *Solar Energy Materials and Solar Cells*, Selected papers of the EMRS 2015 Spring meeting – Symposium C on Advanced Inorganic Materials and Structures for Photovoltaics, 145, Part 2 (February): 109–15. https://doi.org/10.1016/j.solmat.2015.08.028.

Heide, J. van der. 2009. “Cost-Efficient Thermophotovoltaic Cells Based on Germanium.” Katholieke Universiteit Leuven.

Heide, J. van der, N. E. Posthuma, G. Flamand, W. Geens, and J. Poortmans. 2009. “Cost-Efficient Thermophotovoltaic Cells Based on Germanium Substrates.” *Solar Energy Materials and Solar Cells* 93 (10): 1810–16. https://doi.org/10.1016/j.solmat.2009.06.017.

Kerr, Mark J., Andres Cuevas, and Ronald A. Sinton. 2001. “Generalized Analysis of Quasi-Steady-State and Transient Decay Open Circuit Voltage Measurements.” *Journal of Applied Physics* 91 (1): 399–404. https://doi.org/10.1063/1.1416134.

Khvostikov, V. P., O. A. Khostikov, E. V. Oliva, V. D. Rumyantsev, M. Z. Shvarts, T. S. Tabarov, and V. M. Andreev. 2002. “Zinc-Diffused InAsSbP/InAs and Ge TPV Cells.” In *Conference Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conference, 2002.*, 943–46. https://doi.org/10.1109/PVSC.2002.1190736.

Lenert, Andrej, David M. Bierman, Youngsuk Nam, Walker R. Chan, Ivan Celanovic, Marin Soljacic, and Evelyn N. Wang. 2014. “A Nanophotonic Solar Thermophotovoltaic Device.” *Nat Nano* 9 (2): 126–30.

López, G., C. Jin, I. Martín, and R. Alcubilla. 2018. “Impact of C-Si Surface Passivating Layer Thickness on n #x002B; Laser-Doped Contacts Based on Silicon Carbide Films.” *IEEE*

Journal of Photovoltaics 8 (4): 976–81. https://doi.org/10.1109/JPHOTOV.2018.2836963.

Miller, D. L., and J. S. Harris. 1980. “Molecular Beam Epitaxial GaAs Heteroface Solar Cell Grown on Ge.” *Applied Physics Letters* 37 (12): 1104–6. https://doi.org/10.1063/1.91889.

Nagashima, Tomonori, Kenichi Okumura, and Masafumi Yamaguchi. 2007. “A Germanium Back Contact Type Thermophotovoltaic Cell.” *AIP Conference Proceedings* 890 (1): 174–81. https://doi.org/10.1063/1.2711734.

Posthuma, N. E., G. Flamand, W. Geens, and J. Poortmans. 2005. “Surface Passivation for Germanium Photovoltaic Cells.” *Solar Energy Materials and Solar Cells* 88 (1): 37–45. https://doi.org/10.1016/j.solmat.2004.10.005.

Posthuma, N. E., J. van der Heide, G. Flamand, and J. Poortmans. 2007. “Emitter Formation and Contact Realization by Diffusion for Germanium Photovoltaic Devices.” *IEEE Transactions on Electron Devices* 54 (5): 1210–15. https://doi.org/10.1109/TED.2007.894610.

Reboud, V., A. Gassenq, J. M. Hartmann, J. Widiez, L. Virot, J. Aubin, K. Guilloy, et al. 2017. “Germanium Based Photonic Components toward a Full Silicon/Germanium Photonic Platform.” *Progress in Crystal Growth and Characterization of Materials* 63 (2): 1–24. https://doi.org/10.1016/j.pcrysgrow.2017.04.004.

R.R. King, A. Boca, W. Hong, and X.-Q. Liu, D. Bhusari, D. Larrabee, K.M. Edmondson, D.C. Law, C.M. Fetzer, S. Mesropian, N.H. Karam. 2009. “Band-Gap-Engineered Architectures for High-Efficiency Multijunction Concentrator Solar Cells.” In . https://doi.org/10.4229/24thEUPVSEC2009-1AO.5.2.

Sanchez, L., S. Lechago, A. Gutierrez, and P. Sanchis. 2016. “Analysis and Design Optimization of a Hybrid VO2/Silicon 2 x 2 Microring Switch.” *IEEE Photonics Journal* 8 (2): 1–9. https://doi.org/10.1109/JPHOT.2016.2551463.

Sze, S.M., and K. K. Ng. n.d. *Physics of Semiconductor Devices*. 3ed ed. John Wiley & Sons.

Toriumi, Akira, and Tomonori Nishimura. 2017. “Germanium CMOS Potential from Material and Process Perspectives: Be More Positive about Germanium.” *Japanese Journal of Applied Physics* 57 (1): 010101. https://doi.org/10.7567/JJAP.57.010101.

Ungaro, Craig, Stephen K. Gray, and Mool C. Gupta. 2015. “Solar Thermophotovoltaic System Using Nanostructures.” *Optics Express* 23 (19): A1149. https://doi.org/10.1364/OE.23.0A1149.

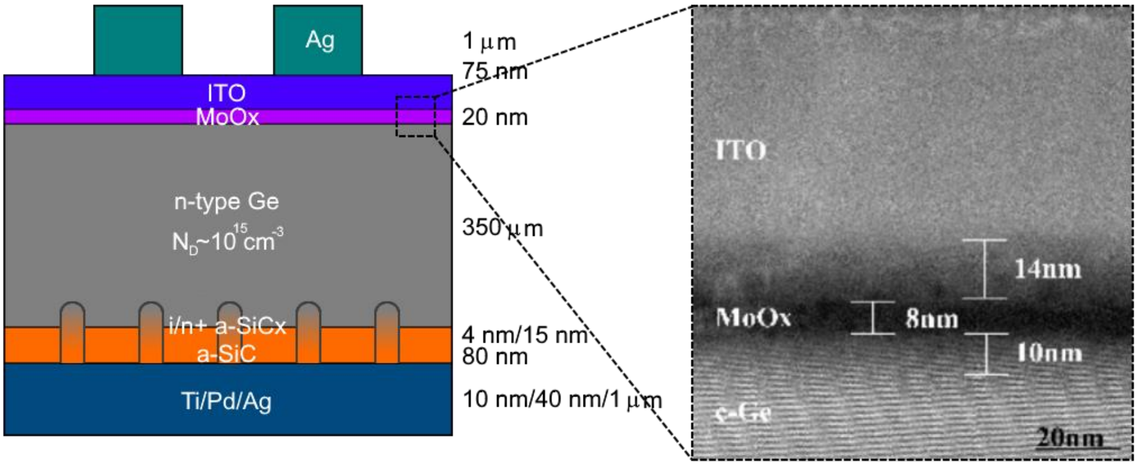

Figure 1. Sketch of the fabricated solar cell. Focus: TEM image of the MoOx interlayer of the final device

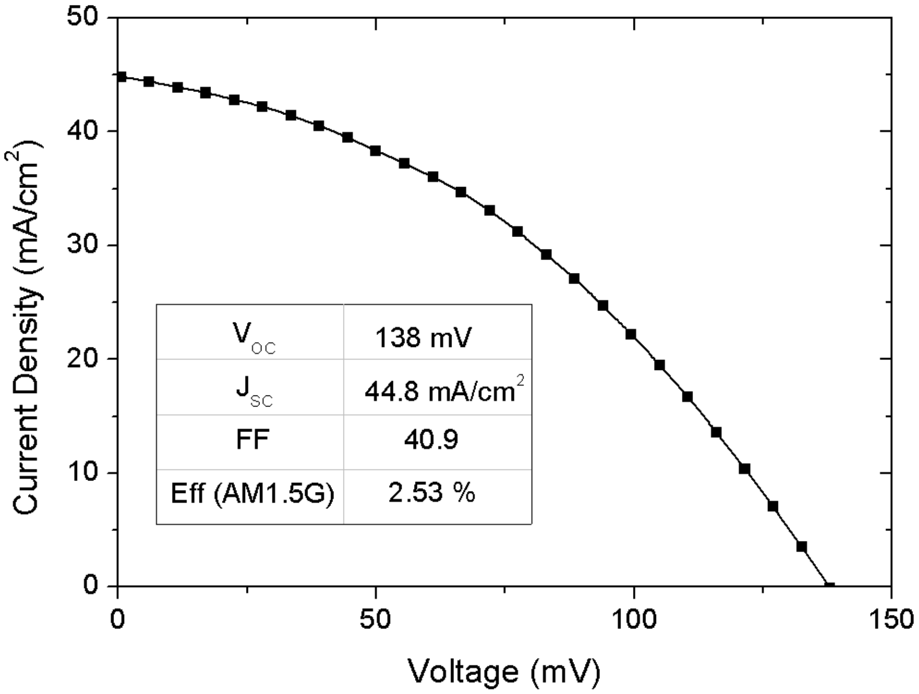

Figure 2. Current density-voltage curve of the Ge PV cell manufactured in this work under AM1.5 G illumination conditions.

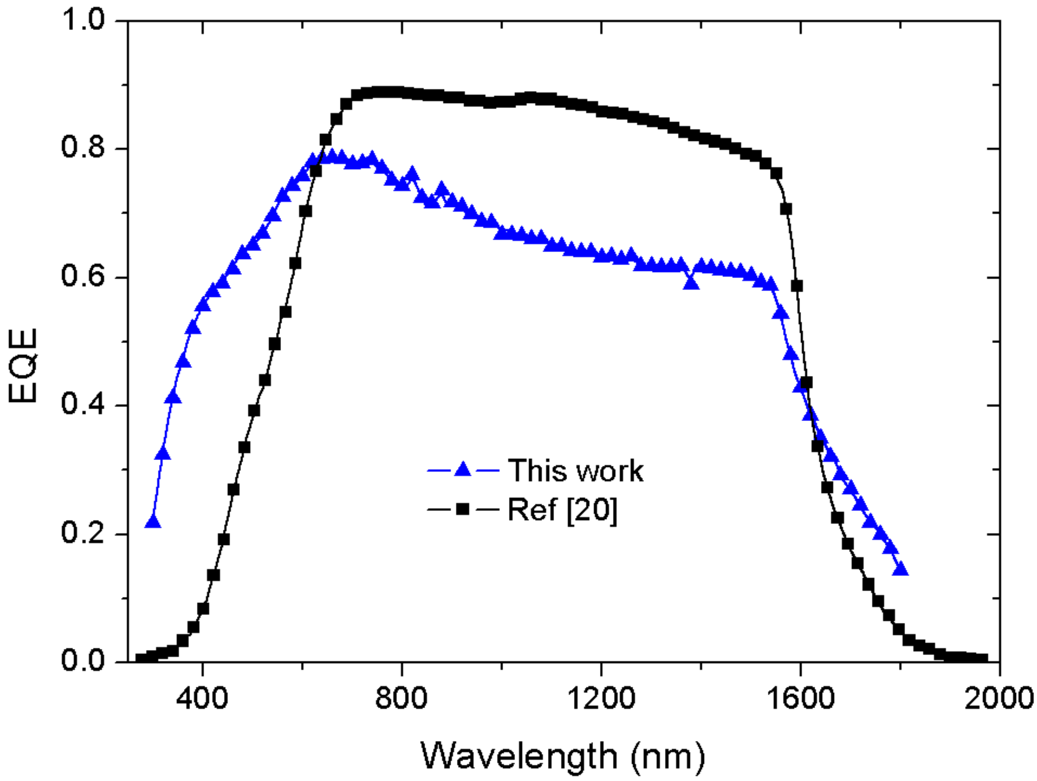

Figure 3. External quantum efficiency of the Ge PV cell manufactured in this work along with that of the Ge PV cell reported in (van der Heide 2009).

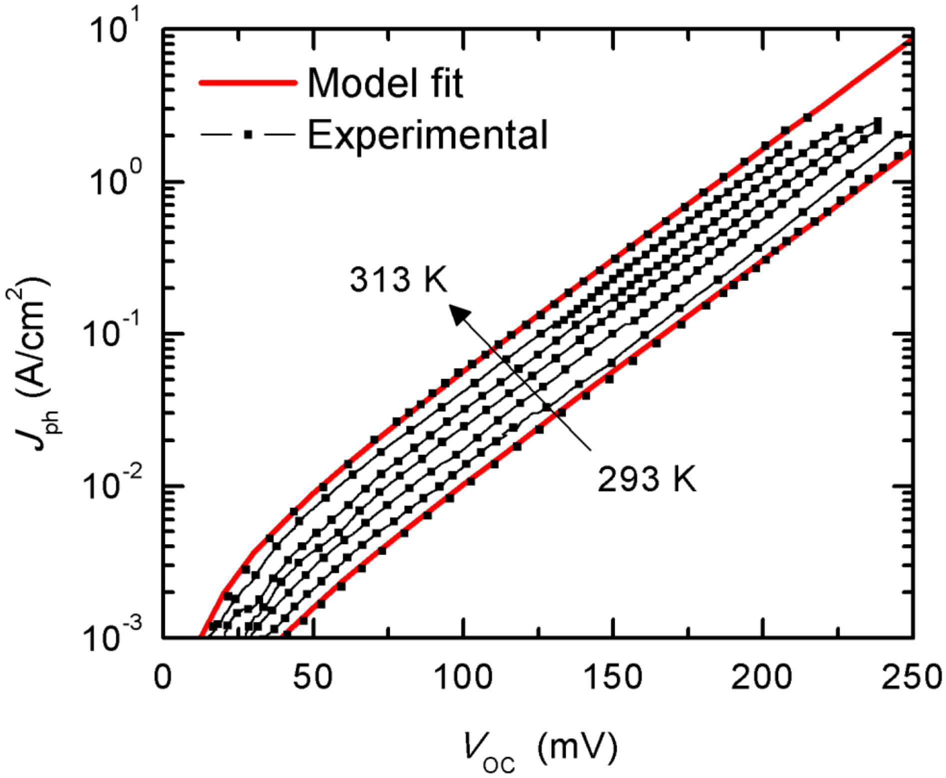

Figure 4. J_{ph}-V_{OC} curves at different temperatures from 293 to 333 K in 5 K steps.

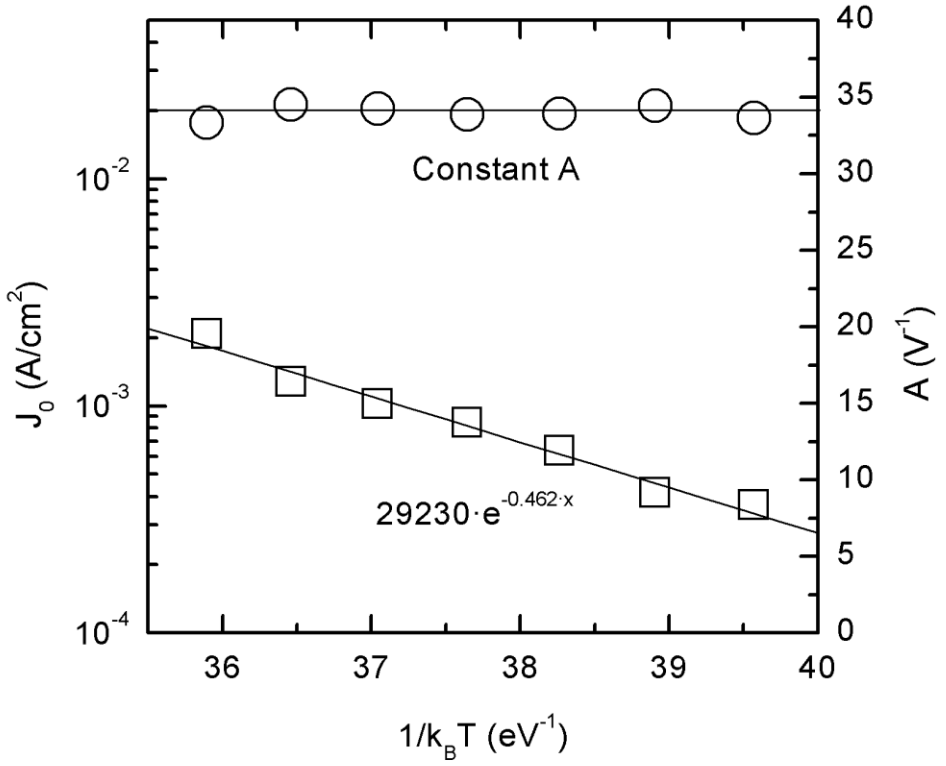

Figure 5. Activation energy and current as a function of temperature