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Enhancing the photovoltaic effect in the infrared region by germanium quantum dots inserted in the intrinsic region of a silicon p-i-n diode with nanostructure

H. M. Tawancy

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Abstract We show that a strong photovoltaic response in the infrared region of the solar spectrum (1.1–1.4 μm wavelength) is obtained by inserting a multilayer structure of germanium quantum dots and silicon spacer layers into the intrinsic region of a silicon p-i-n diode. The multilayer structure (active layer) is deposited on an n-type silicon wafer using the technique of ultra-high vacuum chemical vapor deposition. Reflection high-energy electron diffraction has been used to in situ monitor the transition from the two-dimensional to three-dimensional growth mode of germanium on silicon. The p-type layer of the diode is formed in situ by doping a layer of silicon with boron. Prototype solar cells have been fabricated in situ to measure the energy conversion efficiency. Photoluminescence spectroscopy has been used to probe the presence of any defect-related energy levels within the band gap, and the quality of the diode is determined from measurement of dark current. Scanning electron microscopy, atomic force microscopy, and transmission/scanning transmission electron microscopy have been used to characterize the structure of the active layer. It is demonstrated that by optimizing the structure of the active layer to minimize recombination of charge carriers in the quantum dots, a short-circuit current of 24 mA/cm^2 and an open-circuit voltage of 0.6 V could be achieved leading to an energy conversion efficiency of about 11.5% corresponding to an active layer with a thickness of 300 nm.

H. M. Tawancy (✉)
Center for Engineering Research, Center of Research Excellence in Corrosion, Research Institute, King Fahd University of Petroleum & Minerals, P. O. Box 1639, Dhahran 31261, Saudi Arabia
e-mail: tawancy@kfupm.edu.sa

Introduction

Despite various attempts to develop solar technology achieving targeted cost and efficiency, current production of electricity is still dominated by the conventional single p–n junction silicon cells, which account for more than 80% of the market. Theoretically, the efficiency of these cells is limited to about 31%, which is known as the Schockley–Queisser limit [1]. In this analysis, the major factor limiting the efficiency is that the absorbed photon energy above the Si band gap energy (1.11 eV) is lost as heat by electron–phonon scattering and subsequent phonon emission as the carriers relax to their respective band gap edges. One viable approach to overcome this difficulty is to use a stack of multiple p–n junctions with band gaps chosen to better match the solar spectrum, and recently an efficiency of about 40% has been achieved with III–V multijunction solar cells [2]. However, these cells are not cost effective because they are built on either expensive III–V substrates, or germanium wafers, which are relatively cheaper but still more expensive than Si wafers. Therefore, most evidence points out that the use of Si wafer as the starting material for growing the active layers remains to be a viable means for reducing cost.

In recent years, there has been more emphasis on developing a new generation of solar cells with active layers having nanostructures [3–6]. The main aim is to increase the energy conversion efficiency and reduce cost. One important approach is to incorporate Ge into the active layer to serve two important functions: (i) it enhances absorption in the infrared region of the solar spectrum because of its relatively lower band gap energy (0.67 eV) compared to Si (1.1 eV), and (ii) it allows the integration of small amounts of III–V compounds by accommodating the lattice mismatch between Si and such

compounds as GaAs. In this approach, use is made of the natural tendency of Ge to form nanoscale defect-free islands or quantum dots during the early stages of deposition on a Si substrate [7]. Formation of such coherent islands is a spontaneous process, which occurs when the thickness of the deposited layer exceeds a critical value (wetting layer) on the nanoscale. This leads to a transition of the growth mode from two-dimensional to three-dimensional. Thermodynamically, the driving force for this spontaneous process is the relief of the built-in elastic strain associated with the lattice mismatch between the deposited layer and substrate (4.3% in the case of Ge deposited on Si), which is known as the Stranski–Krastanov growth mode [7]. Although such self-assembled quantum dots exhibit broad distribution in both size and position, it has been shown that starting from a single layer with inhomogeneous dots, it is possible to greatly improve the dot size uniformity by growing multilayer structures consisting of successive layers of Ge dots separated by nanosized Si spacer layers [8, 9]. Another feature of such structures is that the quantum dots in different layers are aligned on top of each other along the growth direction [10]. It is generally accepted that the mechanism underlying such vertical alignments of the quantum dots arises from the elastic strain field created by the Ge quantum dots and mediated by the Si spacer layers [11, 12].

Because of the enhanced near-infrared absorption by Ge (1.1–1.4 μm wavelength), attempts have been made to improve the performance of Si-based solar cells by incorporating Ge quantum dots in the intrinsic region of p-i-n diode made of Si, however, the results remain to be inconclusive. Although in one study, an enhanced photovoltaic response has not been clearly observed [13]; in another study the quantum efficiency is found to slightly increase with the number multiple stacks of Ge dots and Si spacer layers [14]. It is to be noted that in these studies, the active layers were grown by the technique of molecular beam epitaxy, which produces lower quality structures in comparison with the technique of ultra-high vacuum chemical vapor deposition [15–17]. Therefore, this study has been undertaken to further explore the potential of incorporating Ge quantum dots into the intrinsic region of a Si p-i-n diode in enhancing the photovoltaic response in the infrared region. Particular emphasis has been placed upon improving the structural quality of the active layers using the technique of ultra-high vacuum chemical vapor deposition. Important structural parameters considered in this study to enhance the short-circuit current include: (i) density of Ge quantum dots, (ii) number of stacks in the multilayer structure of the active layer, and (iii) thickness of the Si spacer layer.

Experimental procedure

Device-quality n-type silicon wafers 10 cm in diameter and 0.5 mm in thickness were used as substrate to deposit the active layers for various tests and also to fabricate prototype solar cells. All wafers were sliced from single-crystal ingot grown along the ⟨001⟩ direction with a resistance of about 0.003 Ω cm as per standard industry practice. Prior to deposition of the active layers, the wafers were cleaned in a solution of $3HCl:1H_2O_2:1H_2O$ by volume. Pure silane (SiH_4) and hydrogen-diluted (10%) germane (GeH_4) were used as gas sources to deposit the active layers using the technique of ultra-high vacuum chemical vapor deposition, which is highly preferred over the technique of molecular beam epitaxy in producing device-quality materials with very low defect density [15–17] required to realize an enhanced photovoltaic response. Other advantages include higher uniformity, lower thermal budget, and more rapid production rate. Initially, a Si buffer layer about 20 nm in thickness was deposited on the wafer surface to mask any residual surface defects. Extensive calibration experiments were carried out to define the optimum processing parameters including: (i) gas flow rate, (ii) gas pressure, (iii) growth temperature, (iv) density of Ge quantum dots, and (iv) thickness of the Si spacer with the objective of minimizing the thermal budget to reduce production cost. Based upon these experiments, a lower and upper growth temperatures of about 550 and 650 °C were identified with corresponding germane pressure of about 10^{-3} Torr. Also, it was important to define a common growth temperature for both Ge quantum dots and Si spacer layers to maintain the lowest possible thermal budget. Although a lower growth temperature was found to be more favorable for deposition of the required density of Ge quantum dots, the kinetics of depositing Si become very sluggish. This problem was overcome by using the catalytic effect of germane on hydrogen desorption [18]. During growth of the active layers, the transition from two-dimensional to three-dimensional growth mode was in situ monitored by reflection high-energy electron diffraction. Photoluminescence spectroscopy was used to evaluate the quality of the active layers particularly the presence of undesirable impurities and defects in the band gap, which can act as recombination centers of the charge carriers degrading the solar cell efficiency. A standard argon Ar+ laser with power density of 400 mW/cm^2 was used in the photoluminescence measurements. Spectral peaks were detected with a liquid nitrogen-cooled Ge photodetector using standard lock-in technique. Electrical measurements to determine the current–voltage characteristics under illumination and in the dark were carried out using a solar simulator. Measurements under illumination were carried out according to the standards defined by ASTM G 173-03

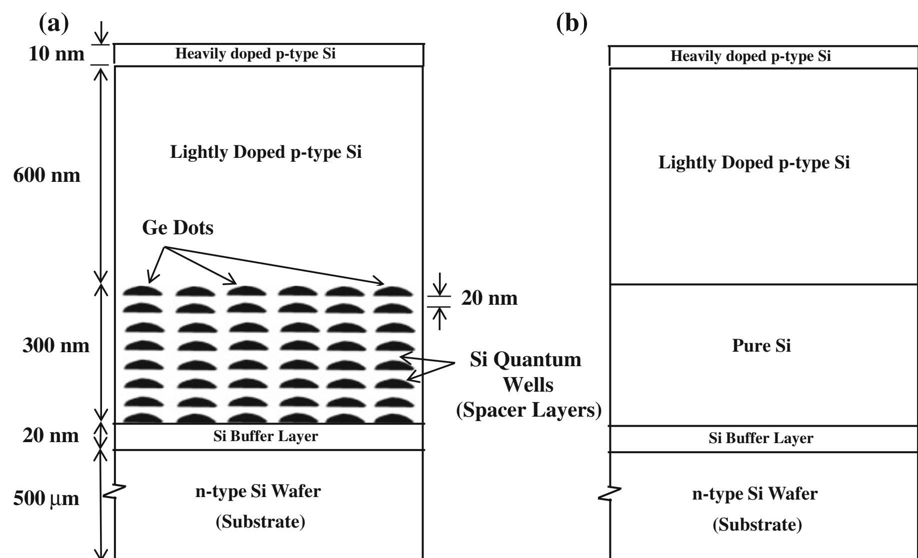

Fig. 1 A schematic illustrating the design of the p-i-n diode used in the study. **a** p-i-n diode containing 300 nm layers of Ge/Si quantum dots in the intrinsic region. **b** Reference diode containing pure Si with the same thickness in the intrinsic region

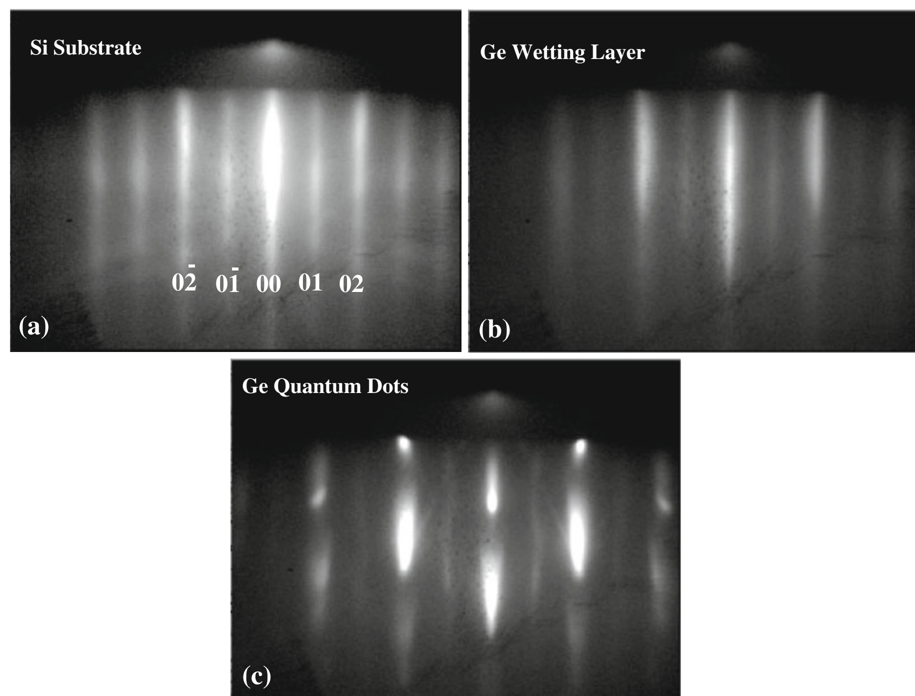

Fig. 2 Examples of reflection high-energy electron diffraction patterns used to in situ monitor the transition from two-dimensional to three-dimensional growth mode of Ge deposited on Si (110 azimuth). **a** Initial Si substrate. **b** Deposition of Ge wetting layer. **c** Formation of Ge quantum dots

(Air Mass 1.5). To measure the dark current, a shutter was used to set the solar cell under dark conditions. Various techniques used to characterize the structure of the active layers included: (i) field emission scanning electron microscopy, (ii) atomic force microscopy, and (iii) transmission and scanning transmission electron microscopy. Specimens for scanning electron microscopy and contact mode of atomic force microscopy were examined in the as-deposited condition. Thin-foils for transmission/scanning transmission electron microscopy were prepared by the focused ion beam technique.

Results and discussion

Based upon the results of calibration experiments an active layer consisting of 15 stacks of Ge quantum dots separated by 15 stacks of Si spacer layers with a total thickness of 300 nm was selected for the present study on the basis of the structural quality as explained later. Figure 1 shows the design scheme of the p-i-n diode. To achieve an electric field across the active layer, the outermost Si spacer layer was topped with a lightly doped layer of p-type Si layer about 600 nm in thickness followed by a thin layer of

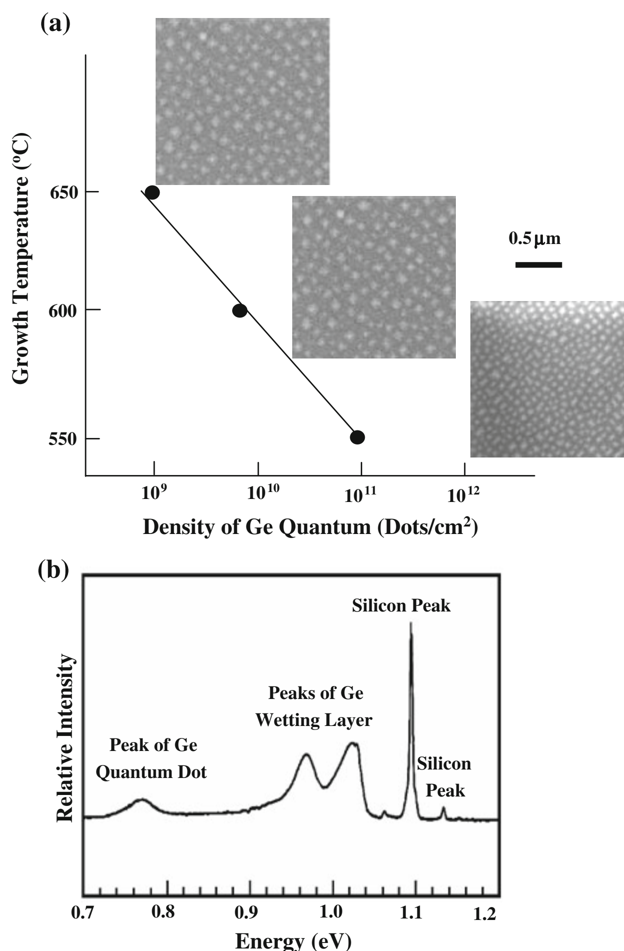

Fig. 3 Density and crystal quality of the Ge quantum dots. **a** Effect of growth temperature at a germane pressure of 10^{-3} Torr on the density of Ge quantum dots shown in the secondary electron SEM images of the *inset*. **b** An example of a corresponding photoluminescence spectrum derived at 11 K

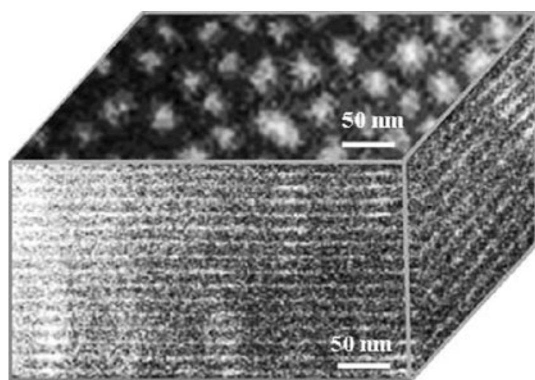

Fig. 4 A composite SEM image showing planar and cross-sectional views of the active layer

heavily doped p-type Si about 10 nm in thickness. For reference purposes, an active layer consisting of pure Si with a thickness of 300 nm was also included in the study (Fig. 1b).

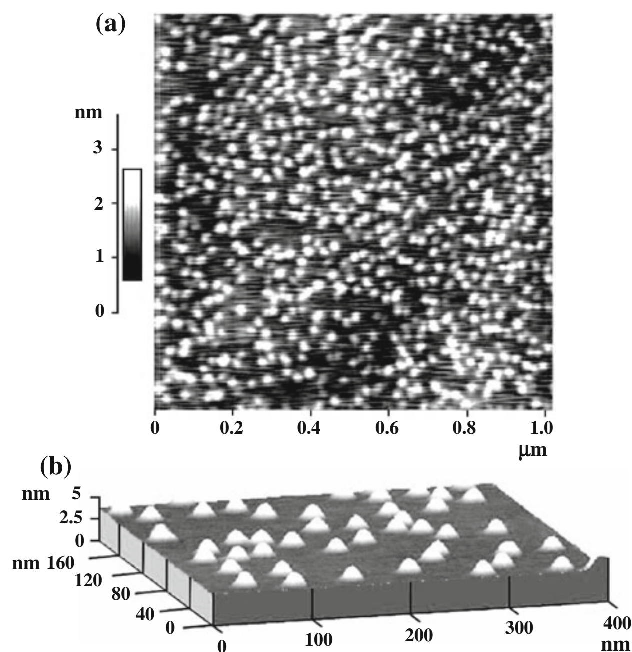

Fig. 5 Atomic force microscopy images illustrating the two-dimensional (**a**) and three-dimensional (**b**) morphology of germanium quantum dots deposited at 500 °C and a germane pressure of 10^{-3} Torr

An important factor considered in this study is the growth time of the active layers in order to maintain a lower thermal budget (temperature level for processing and fabrication of the solar cell device) and in turn, a lower cost. Generally, a growth time of 8 h or less is considered to be reasonable by standard industry practice [17]. Also, of equal importance is to be able to grow both the Ge quantum dots and Si spacer layers at the same temperature in order to reduce the total growth time. Optimizing important structural parameters particularly: (i) density of Ge quantum dots, (ii) number of stacks in the multilayer structure, and (iii) thickness of the Si spacer layer is of utmost importance in enhancing the short-circuit current to offset the reduction in open-circuit voltage caused by the relatively low band gap energy of Ge. Toward the objective of maximizing the short-circuit current, it is essential that the dark current generated in the p-i-n diode is maintained at a level in the picoampere range (10^{-12}) at a reverse bias of −1 V [19]. This was in the present study by adjusting the density of Ge quantum dots, number of stacks in the multilayer structure, and thickness of the Si spacer layer as demonstrated later.

Examples of reflection high-energy electron diffraction patterns derived in situ from the wafer surface to monitor the transition from two-dimensional to three-dimensional growth mode of Ge are shown in Fig. 2. Prior to deposition, the thin surface layer of Si contributing to the diffraction pattern gives rise to streaked Bragg reflections as

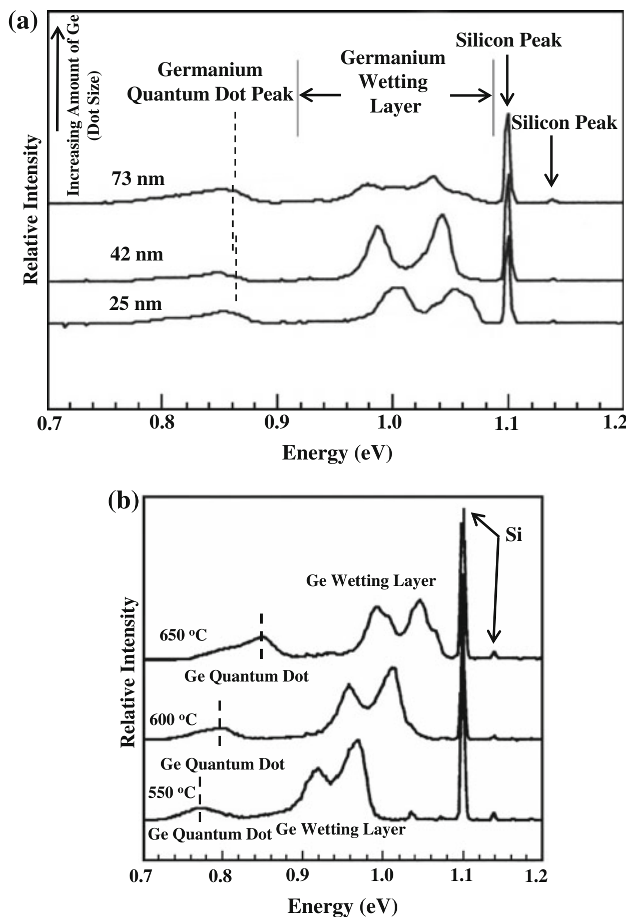

Fig. 6 Photoluminescence spectra derived at 11 K to illustrate characteristic optical properties of the germanium quantum dots. **a** A spectra illustrating the effect of dot size on the characteristic energies for a growth temperature of 550 °C. **b** Spectra derived for various growth temperatures at the onset of two-dimensional to three-dimensional growth of the germanium dots

shown in Fig. 2a. The weaker streaked reflections in Fig. 2b correspond to the Ge wetting layer. Transition from the two-dimensional to three-dimensional growth mode is indicated by formation of discrete reflections (spots) as shown in Fig. 2c.

Figure 3a shows the effect growth temperature in the range of 550–650 °C at a germane pressure of 10^{-3} Torr on the density of Ge quantum dots shown in the secondary electron SEM images of the inset. It is observed that the dot density has increased from about 4×10^{9}/cm^{2} to 10^{11}/cm^{2} with a corresponding reduction in dot diameter from about 90–25 nm as the growth temperature is reduced from 650 to 550 °C. The high crystal quality of the Ge quantum dots is demonstrated in the photoluminescence spectrum of Fig. 3b. Absence of defect-related energy levels indicate that holes captured by the Ge quantum dots are confined there and recombine with electrons in the Si spacer layer radiatively without considerable loss by nonradiative recombination. A

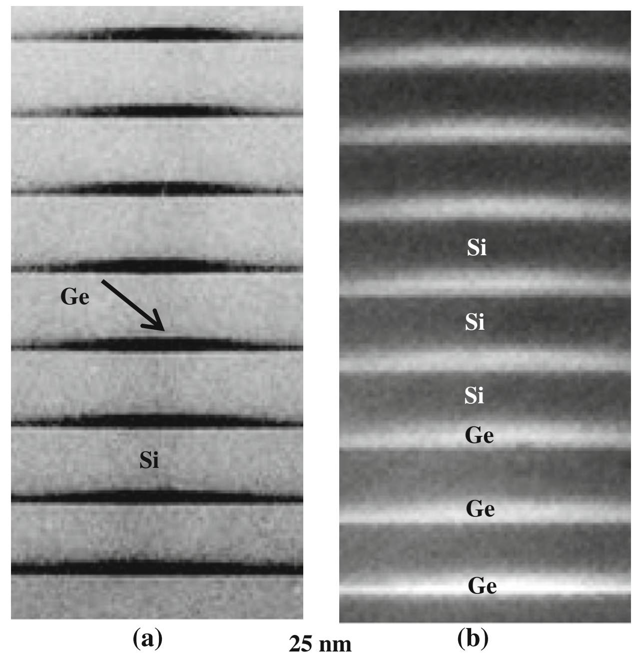

Fig. 7 Structural features of the active layer grown at 550 °C on the scale of transmission/scanning transmission electron microscopy. **a** Bright-field transmission image showing vertical ordering of the germanium dots beneath the Si space layers. **b** A corresponding Z-contrast image derived in the scanning transmission mode

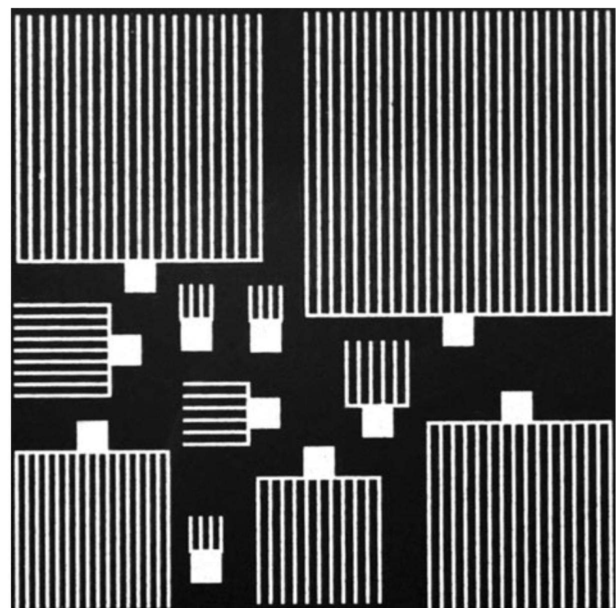

Fig. 8 A photograph showing the front fingers of a typical solar cell fabricated on a silicon wafer

composite SEM image showing planar and cross-sectional views of the active layer is illustrated in Fig. 4. As shown in the high-magnification image parallel to the surface, the Ge quantum dots assume a broad dome-type morphology. Vertical ordering of the dots and their uniformity in size are

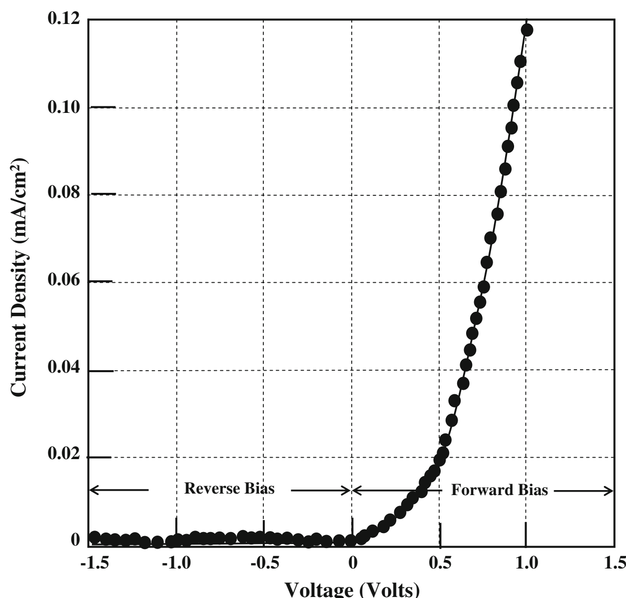

Fig. 9 Current–voltage diagram derived from the Ge/Si solar cell in the dark under forward and reverse bias

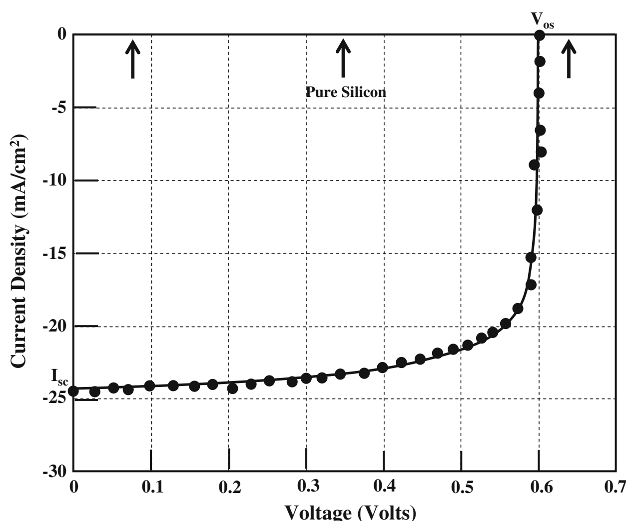

Fig. 10 Current–voltage characteristics derived from the Ge/Si and pure Si cells under standard illumination conditions. The short-circuit current I_{sc} and open-circuit voltage V_{os} of the Ge/Si solar cell are indicated

indicated in the cross-sectional view. These results are further verified on the finer scales of atomic force microscopy and high-resolution transmission and scanning/transmission electron microscopy as described below.

Figure 5a shows an AFM image (scanned area = 1 μm²) of the Ge quantum dots deposited at 550 °C with a density of about 10^{11}/cm². As shown in the inset, the distance moved by the sensor along the *z*-direction indicates that the dot height is about 2 nm. This is further verified in the three-dimensional image of Fig. 5b demonstrating the broad dome-type morphology of the dots. In this case, the size of

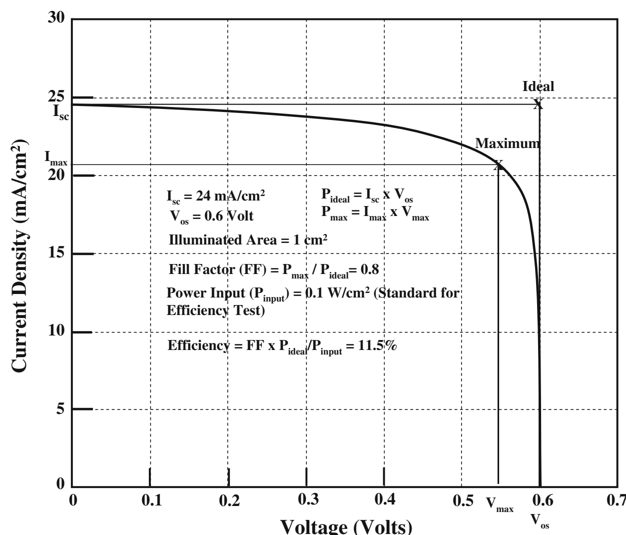

Fig. 11 Current–voltage data of the Ge/Si solar cell of Fig. 10 plotted according to the standard used by manufacturers of solar cells to calculate the energy conversion efficiency

the dots has very little or no effect on the positions of energy peaks in photoluminescence spectra as demonstrated in Fig. 6a. This is in contrast to the case of quantum dots of other semiconductors such as GaAs and InAs [20]. However, the characteristic energies of the spectra are found to be dependent upon the growth temperature as shown in the spectrum of Fig. 6b derived at the onset of the transition from two-dimensional to three-dimensional growth mode so that the dot size is fixed as monitored by reflection high-energy electron diffraction Therefore, electron confinement of the Ge quantum dots becomes more controlled by the dot height. In the meantime, the results suggest that the characteristic energies of the photoluminescence spectra are more dependent upon interdiffusion between Ge and Si during growth of the active layer leading to a change in the band gap energy.

Examples illustrating the results of analyzing the structure of the active layer grown at 550 °C by transmission and scanning/transmission electron microscopy are shown in Fig. 7. Vertical alignment of the Ge quantum dots is evident in the bright-field image of Fig. 7a as well as the Z-contrast image of Fig. 7b. As can be seen, the thickness of the Si spacer layer is maintained at about 20 nm. This allows vertical transport of charge carriers between densely stacked Ge quantum dots by strong electronic coupling with the effects of enhancing the photocurrent and minimizing the tendency for recombination of electrons and holes within the Ge quantum dots [21, 22]. Thicker Si layers are found to preclude vertical alignment of the Ge quantum dots reducing charge mobility. In the meantime, a too thin layer is also undesirable because it can lead to interaction between Ge quantum dots in different layers causing the formation of defects, which degrade the device performance.

Based upon the above results, prototype solar cells have been fabricated with active layers consisting of 15 stacks of Ge quantum dots (areal density of about $10^{11}/cm^2$) and 15 stacks of Si spacer layers (layer thickness of about 20 nm) all grown at 550 °C. For comparative purposes, solar cells with active layers of pure Si with the same thickness have also been fabricated. After deposition of the respective layers, fabrication of the solar cells was completed in situ by forming back contact using front finger made of a standard Au–Ti alloy consisting of 5 nm Ti and 400 nm Au layers. A photograph showing the front fingers of a representative solar cell is shown in Fig. 8.

Figure 9 illustrates the current–voltage characteristics of the solar cell made with Ge/Si multilayer structure in the dark. It is observed that at a reverse bias or negative potential of -1 V, the dark current approaches 0 consistent with the behavior of a p-i-n diode. In contrast, a high current is obtained under the influence of a forward bias or positive potential as required by as required by high quality diode consistent with the high structural quality of the active layer demonstrated by the results presented earlier. Comparative photovoltaic response under standard illumination conditions for the infrared region of the Ge/Si and pure Si cells is shown current–voltage data of Fig. 10. As can be seen, no current could be detected in the case of the pure Si cell. In contrast, a strong photovoltaic response is obtained in the case of the Ge/Si cell providing a short-circuit current density of about 24 mA/cm^2 and an open-circuit voltage about 0.6 V.

Using the data of Fig. 10, the energy conversion efficiency of the Ge/Si cell with a 300 nm active layer has been calculated to be about 11.5% as summarized in Fig. 11. Details about the procedure for calculating the energy conversion efficiency can be found in several references, e.g., [23]. The efficiency $\eta = \mathrm{FF}\ (P_{\mathrm{ideal}}/P_{\mathrm{input}})$ where FF is the fill factor corresponding to the ratio of the outlined rectangular areas in Fig. 11. These are identified by the points labeled maximum and ideal (P_{ideal} is the product of the short-circuit current and open-circuit voltage) and $P_{\max}$ is the maximum power realized corresponding to the largest rectangular area enclosed by the I–V diagram corresponding to the point of maximum power as shown. As per standard test condition, the power input (energy of the incident radiation) $P_{\mathrm{input}} = 0.1$ Watt/m^2.

Conclusions

It is concluded from the results of this study that a strong photovoltaic response can be obtained by inserting a nanostructured multilayer of germanium quantum dots and silicon spacer layers into the intrinsic region of a silicon p-i-n diode. This can be achieved by optimizing the structure of the active layer particularly the density of quantum dots, thickness of the silicon spacer layer, and number of stacks in the multilayer structure in order to minimize recombination of charge carriers in the quantum dots. Prototype solar cells designed on the basis of such multilayer structure with a thickness of only 300 nm have an energy conversion efficiency of about 11.5% indicating that incorporating germanium quantum dots into silicon-based solar cells can have a high potential in developing solar technology achieving targeted cost and efficiency.

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