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EFFECT OF SUBSTRATE MODIFICATION ON PROPERTIES OF THERMALLY EVAPORATED BARIUM DISILICIDE THIN-FILMS

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Abstract: Orthorhombic $BaSi_2$ films were grown successfully on flat and modified Ge substrates the by thermal evaporation method at 500 ºC with an a-Si supply layer. The obtained results showed that within a short etching time t_e (less than 15 min), the substrate modification had a negligible impact on improving the crystalline quality and optical properties of the $BaSi_2$ films in comparison with using flat substrate. When t_e is 15 min, the crystalline quality as well as optical properties were improved significantly. However, the crystalline quality degraded whereas the optical properties was still improved as t_e > 15 min. Therefore, we chose t_e of 15 min as the optimized condition for surface modification of Ge substrate. Photoresponse properties of evaporated $BaSi_2$ films on modified (with t_e = 15 min) and flat Ge substrates showed that the film grown on the former has better properties than that on the latter. We also confirmed the bandgap of thermally-evaporated $BaSi_2$ films at 1.29 eV. These results suggest the potential application of the $BaSi_2$ thin-film evaporated on modified Ge substrate as an absorber for thin-film solar cells.

Key words: Barium disilicide; Silicide semiconductor; thermal evaporation; substrate modification; optical property; photoresponse; Ge substrate.

1. Introduction

A solar cell is known as a device that converts sunlight directly into electrical energy. At present, silicon (Si) is the most used material in solar cell manufacturing thanks to some of its remarkable features, such as safety, stability, and earth-abundance. However, this material has two main drawbacks, which are high manufacturing costs due to the required thick film and a slightly small band-gap for a single-junction solar cell [1]. In order to overcome these drawbacks, other semiconductors such as cadmium telluride (CdTe) [2, 3] and copper indium gallium diselenide (CIGS) [4, 5] have received much attention. Thin-film solar cells based on these semiconductors have already been commercialized. However, these materials still cannot meet the global deployment due to the lack of some important properties such as earth-abundant, environment-friendly, and inexpensive components. Therefore, it is necessary to explore new or alternative materials which meet all of the requirements for state-of-the-art solar cell applications. Barium disilicide ($BaSi_2$) is a promising candidate thanks to its remarkable features such as abundant and inexpensive components of Ba and Si, a suitable band gap of approximately 1.3 eV [6-11], high absorption coefficient (~3×10^4 cm^{-1} at 1.5 eV) [9, 11, 12], long minority carrier diffusion length and lifetime (~10 µm and ~14 µs, respectively) [13, 14]. At atmospheric pressure, orthorhombic $BaSi_2$ is the most suitable structure for utilization in photovoltaics [15].

For practical application of $BaSi_2$ on large-scale area, thermal evaporation (TE) is a suitable method. This is because TE is the simple method which can reduce the deposition time thanks to the high deposition rate and still ensure to produce the uniform thin-film. Using the TE method, the $BaSi_2$ thin-film was successfully grown on various flat substrates such as Si [16 - 18], glass [12], CaF_2 [19], and Ge [20]. Using Ge as a substrate for growing $BaSi_2$ has some advantages. Firstly, the thermal

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expansion coefficient of Ge is close to that of $BaSi_2$, which may reduce cracks formation in $BaSi_2$ grown at high temperature. Secondly, $BaSi_2$/Ge heterojunction solar cells might absorb light in a wide wavelength range due to the small band gap of Ge. Modifying the substrate surface before growing $BaSi_2$ has an impact on reducing light reflection and increasing absorption, which is a key issue in improving optoelectronic device performance.

In this study, we worked on the Ge substrate and modified its surface by means of a simple method. Since the vapor composition produced from $BaSi_2$ source is Ba-rich at the initial stage [12, 16], it is necessary to supply Si atoms at this stage to achieve stoichiometric $BaSi_2$ film. Therefore, an amorphous Si (a-Si) supply layer is deposited prior to the growth of $BaSi_2$ film. The purpose of this study is to grow and characterize properties of orthorhombic $BaSi_2$ films on modified Ge substrates. In order to show the advantage of substrate modification, we compare the properties of $BaSi_2$ grown on modified substrates with those on flat ones. The substrate modification condition is also optimized.

2. Experimental procedure

P-type (100) Ge (ρ = 1–10 Ω·cm) substrates, after having been cleaned with acetone and deionized water (DI), were dipped into a diluted HNO_3 (70%) solution to form domes on the surface. The dipping time varied from 5 to 20 mins. Then, the substrates were dipped into a diluted HF (5%) solution for 3 min to remove the oxide layer. After cleaning with DI water, the substrates were loaded into a RF sputtering chamber for deposition of a 50 nm-thick-a-Si supply layer at a substrate temperature of 300 ^{o}C. After that, 200 nm-thick-$BaSi_2$ films were evaporated at a substrate temperature of 500 ^{o}C and a base pressure of 1.0×10^{-5} mbar. For comparison, $BaSi_2$ films were also grown on flat substrates under the same condition. Figure 1 shows cross-sectional illustrations of the fabricated $BaSi_2$ films on modified and flat Ge substrates.

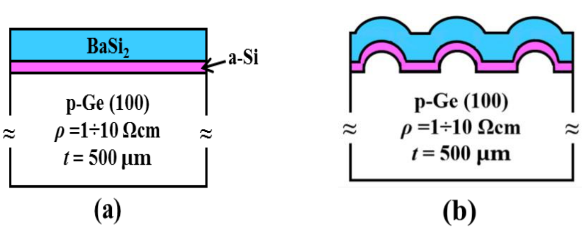

Figure 1. *Cross-sectional illustrations of the fabricated $BaSi_2$ films on (a) flat and (b) modified Ge substrates*

Surface and interface morphologies as well as thickness of the evaporated film were observed by scanning electron microscopy (SEM; JEOL JSM-7001-FA). The crystalline property of $BaSi_2$ films was estimated by means of Raman spectroscopy (Tokyo Instruments Nanofinder) using Ar^+ ion laser with an excitation wavelength of 488 nm. For optical properties characterization, we employed a JASCO Ubest V-570 spectrophotometer to obtain the reflectance (R) and transmittance (T) spectra from the samples. The absorptance (A) spectra were obtained using $A = 1 - R - T$. In order to investigate the vertical photocurrent, an 80-nm-thick indium tin oxide (ITO) and 200-nm-thick Al were deposited on the surface of the $BaSi_2$ film and the backside of Ge substrate, respectively. The photocurrent was measured by a lock-in technique using a 450 W xenon and 400 W halogen lamps with a monochromator to produce a monochromatic light with a constant power of 50 μW/cm^2.

3.Results and discussions

Figure 2 shows the SEM side and cross-sectional views of the evaporated $BaSi_2$ films on flat and modified Ge substrates at various etching times t_e. In Fig. 2(a), it can be seen that the evaporated $BaSi_2$ film has a smooth surface and no crack formation on the surface as well as along the thickness. For the films grown on modified substrates, the dome morphology of Ge substrate after the evaporation of $BaSi_2$ films remains the same as before. The a-Si supply layer is almost consumed, which reveals the relatively smooth and clear $BaSi_2$/Ge interface for all of the samples. As shown in the insets of Figs. 2(b)-(e), the height and diameter of the domes increase with t_e. At t_e of 20 min, the $BaSi_2$ film surface becomes rough due to the increase in porosity. Under the same evaporation condition of $BaSi_2$ film, the higher and larger domes were, the larger $BaSi_2$/Ge interface area and more porous $BaSi_2$ film were obtained. The large interface area can reduce the in-plane film stress which is the cause of micro-crack formation when evaporating at high temperature [12,18] but increase the porosity (and thus crystal defects) of the film. Therefore, we should consider the trade-off between them and optimize t_e when employing the modified substrate.

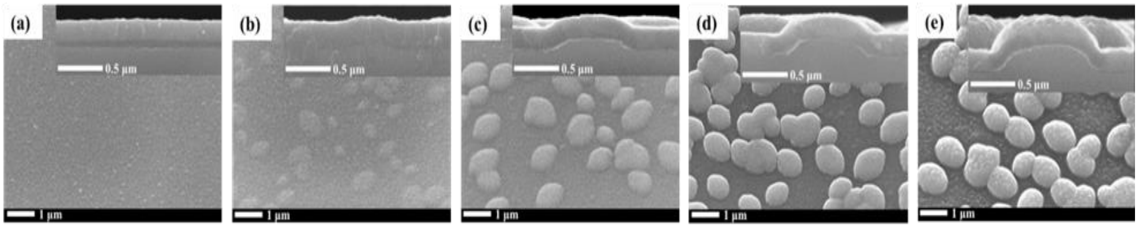

Figure 2. *SEM side and cross-sectional views of $BaSi_2$ films grown on (a) flat and modified Ge substrates at different etching times: (b) 5 min, (c) 10 min, (d) 15 min, and (e) 20 min*

The Raman spectra of the evaporated $BaSi_2$ films on flat and modified Ge substrates at various t_e are shown in Fig. 3(a). The observed peaks are identified as the vibration modes of $[Si_4]^{4-}$ anion in $BaSi_2$, suggesting that all films are orthorhombic $BaSi_2$ [21-24]. Figure 3(b) shows the full width at half-maximum (FWHM) values of A_1 mode, which are used as a measure of crystalline quality. The lower value of FWHM, the better crystalline quality of the film. It can be seen that FWHMs of the films on the modified substrates are smaller than that on the flat one, indicating that the films grown on the former have a better quality than that on the latter. It can be explained by the reduction of the film stress when evaporating on the modified substrates at a high temperature due to the increase in interface area, in comparison with evaporating on the flat substrate. For the films grown on the modified substrates, FWHM seems to be unchanged with t_e until 10 min, suggesting that 10 min is not a critical t_e for improving crystalline quality. FWHM, then, decreases with t_e up to 15 min and increases beyond it. This suggests that 15 min is the optimum t_e for the modification of the Ge substrate in improving crystalline quality of the evaporated $BaSi_2$. At the longer etching time (i.e. t_e = 20 min), due to the increase in porosity and therefore crystal defects as mentioned previously, the crystalline quality of the film begins to degrade.

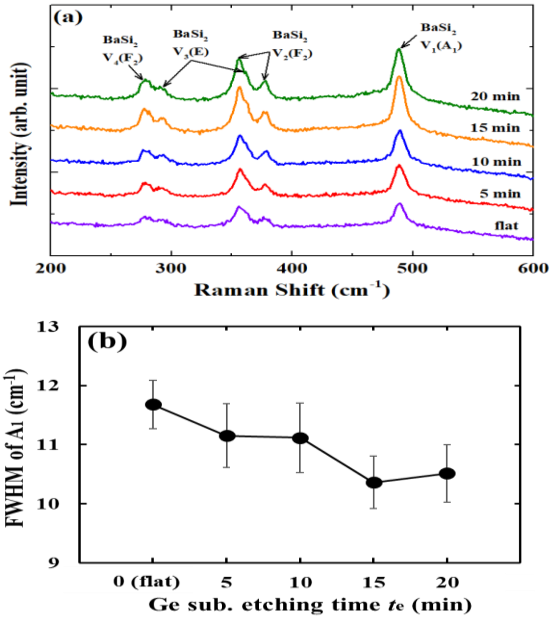

Figure 3. *(a) Raman spectra and (b) FWHM of A_1 mode of $BaSi_2$ films grown on flat and modified Ge substrates at various t_e*

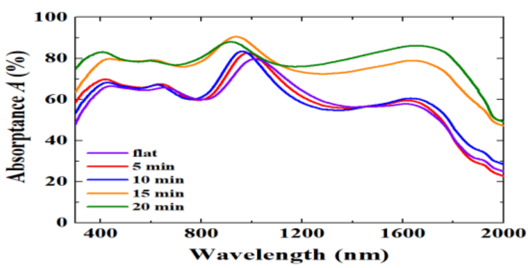

Figure 4. *Absorptance A spectra of $BaSi_2$ films grown on flat and modified Ge substrates*

Figure 4 shows the absorptance *A* spectra of the evaporated $BaSi_2$ films on flat and modified Ge substrates at various t_e. It is obvious that *A*s of the films with t_e of 5 and 10 mins are almost the same as that on flat substrate. This indicates that the slight substrate modification has no effect on increasing the absorption of $BaSi_2$ films. On the other hand, *A*s of the films grown with t_e of 15 and 20 mins are higher than that on flat substrate. This suggests that the light trapping effect works well when t_e is equal or more than 15 min.

From the above results, etching time was optimized at 15min, considering the trade-off between crystalline quality and optical properties.

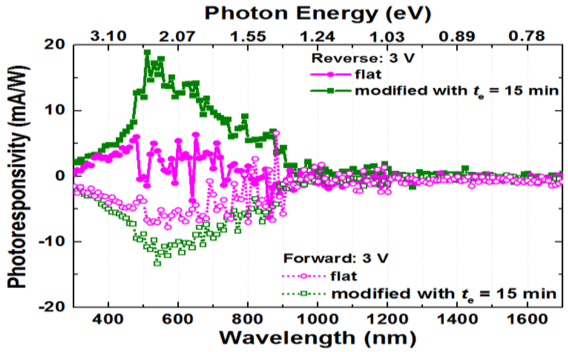

Figure 5. *Photoresponse spectra of ITO/$BaSi_2$/p-Ge (modified with t_e = 15 min and flat)/Al structures under forward and reverse bias voltages of 3 V*

Figure 5 shows the photoresponse properties of ITO/$BaSi_2$/p-Ge (modified with t_e = 15 min and flat)/Al structures under forward and reverse bias voltages of 3 V. The photocurrent is generated by the light absorption and electron-hole pairs separation by electric field. For $BaSi_2$/modified Ge, the photoresponsivity can be observed clearly whereas that for $BaSi_2$/flat Ge is very weak and noisy. This suggests that the crystalline quality and/or interface property of $BaSi_2$/modified Ge is better than that of $BaSi_2$/flat Ge. It can be explained by the increase in interface area and reduction of film stress when evaporating $BaSi_2$ on modified Ge at high temperature in comparison with that on flat Ge as mentioned previously. The result is confirmed by Raman spectra analysis. Moreover, the result also shows the effect of substrate modification on enhancing the absorption by light trapping, which is confirmed by optical properties measurement. The onset of photocurrent is at photon energy of 1.29 eV, which is supposed as the band-gap value of $BaSi_2$.

4. Conclusion

Orthorhombic $BaSi_2$ films were grown successfully on flat and modified Ge substrates by the TE method at 500 °C with an a-Si supply layer. The obtained results showed that, at short etching time t_e (less than 15 min), the substrate modification had a negligible impact on improving the crystalline quality and optical properties of the $BaSi_2$ films in comparison with using a flat substrate. When t_e is 15 min, the crystalline quality as well as optical properties was improved significantly. Therefore, we chose t_e of 15 min as the optimized condition for surface modification of Ge substrate. Photoresponse properties of evaporated $BaSi_2$ films on modified (with t_e = 15 min) and flat Ge substrates showed that the film grown on the former had better properties than that on the latter. We also confirmed the bandgap of thermally-evaporated $BaSi_2$ films at 1.29 eV. These results suggest the potential application of the $BaSi_2$ thin-film be evaporated on modified Ge substrate as an absorber for thin-film solar cells.

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ẢNH HƯỞNG CỦA SỰ ĐIỀU CHỈNH ĐẾ ĐẾN CÁC TÍNH CHẤT CỦA MÀNG MỎNG BARI ĐISILIC BỐC BAY NHIỆT

Tóm tắt: Trong nghiên cứu này, chúng tôi đã chế tạo thành công màng mỏng $BaSi_2$ có cấu trúc tinh thể hệ thoi trên đế Ge phẳng và đế Ge được điều chỉnh bằng phương pháp bốc bay nhiệt ở 500 ^oC sử dụng lớp cung cấp nguyên tử Si. Các kết quả đạt được cho thấy, với thời gian điều chỉnh đế t_e ngắn (nhỏ hơn 15 phút), sự điều chỉnh đế không có tác dụng đáng kể trong việc cải thiện chất lượng kết tinh và các tính chất quang học của màng $BaSi_2$ so với dùng đế phẳng. Khi t_e = 15 phút, chất lượng kết tinh cũng như các tính chất quang được cải thiện đáng kể. Tuy nhiên, chất lượng kết tinh bị suy giảm trong khi các tính chất quang vẫn được cải thiện khi t_e > 15 phút. Vì thế, chúng tôi chọn t_e = 15 phút là thời gian tối ưu cho sự điều chỉnh bề mặt đế Ge. Các tính chất hồi đáp quang học của màng $BaSi_2$ trên đế Ge được điều chỉnh (với t_e = 15 phút) và trên đế Ge phẳng cho thấy màng chế tạo trên đế được điều chỉnh có tính chất tốt hơn so với trên đế phẳng. Từ phép đo hồi đáp quang học, chúng tôi cũng xác định được vùng cấm của $BaSi_2$ là 1,29 eV. Các kết quả này gợi mở tiềm năng ứng dụng của màng mỏng $BaSi_2$ bốc bay trên đế Ge được điều chỉnh như là chất hấp thụ trong chế tạo pin mặt trời.

Từ khóa: Bari Đisilic; bán dẫn hợp chất với silic; bốc bay nhiệt; sự điều chỉnh đế; tính chất quang học; hồi đáp quang học; đế Ge.