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Effects of Amorphous Si Capping Layer on Sputtered BaSi₂ Film Properties

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Regarded as a promising absorber material for solar cell applications, Barium disilicide (BaSi₂) is still confronted with issues related to surface oxidation. Here, we use a-Si:H deposited by plasma-enhanced chemical vapor deposition as capping layer to prevent surface oxidation of sputtered BaSi₂ films. Based on crystalline quality and optical properties characterizations, thin a-Si:H capping cannot sufficiently prevent surface oxidation. Conversely, oxidation of a-Si:H layer in turn promotes Ba diffusion and Si isolation. Applying a thicker a-Si:H capping layer (more than 20 nm) can suppress such effect. The multi-materials capping layer can also be regarded as potential strategy to prevent surface oxidation of BaSi₂.

1. Introduction

Barium disilicide (BaSi₂) has been regarded as a promising light-absorbing material for high-performance thin-film solar cells [1]. The semiconducting BaSi₂ is orthorhombic and stable in the ambient condition [2], exhibits an unintentionally n-type conductivity [3], and possesses a suitable band gap ($E_g = \sim 1.3$ eV) for solar energy conversion [4]. Besides, it also holds attractive optical and electrical properties, i.e., a high light absorption coefficient (α) reaching 10^5 cm⁻¹ for photon energy $h\nu > 1.5$ eV, a long minority carrier lifetime τ (~ 27 μ s) [5], and essentially elemental abundance and non-toxicity. Theoretically, the attainable conversion efficiency (η) of BaSi₂ homojunction solar cells is up to 25% [6]. However, BaSi₂ is confronted with the issue of surface oxidation due to its reactivity with oxygen and moisture. The formed oxide layer hinders the carrier transport. Additionally, the oxidation-induced structure transformation phenomenon has been revealed by our previous research, which alters the stoichiometry, results in defective phases, and further degrades the film quality [7]. Hence, it is essential to develop anti-oxidation layer to improve the quality of thin-film BaSi₂. Amorphous Si (a-Si) capping layer has been applied to suppress surface oxidation of BaSi₂ films, which additionally improves both electrical and optical properties of the material [8].

In this contribution, hydrogenated amorphous silicon (a-Si:H) is utilized as capping layer on sputtered BaSi₂ thin films. Property comparisons between a-Si:H/BaSi₂ structure and bare BaSi₂ are presented and further analyzed. Influences of a-Si:H capping layer thickness are also discussed.

2. Experimental

A Kurt J. Lesker radio-frequency magnetron sputtering set-up with a stoichiometric ceramic BaSi₂ target was deployed for the deposition of BaSi₂ films. Prior to the growth, a pre-sputtering process was carried out for 10 min. BaSi₂ films were deposited on fused silica substrates. After sputtering, a-Si:H capping layers were deposited by means of an Elettrorava

plasma-enhanced chemical vapor deposition equipment. Samples were then annealed for 90 min in a nitrogen atmosphere. Annealing temperatures (T_a) ranged from 600 to 750 °C.

Raman spectra were acquired by an InVia Raman Microscopy (Renishaw) set-up with an excitation wavelength of 633 nm. The wavelength-dependent reflectance and transmittance (R/T) were measured by a PerkinElmer Lambda 950 spectrometer. The surface morphology and roughness of samples were characterized and analyzed by atomic force microscopy (AFM, NT-MDT). The thickness of a-Si:H ($d_{a-Si:H}$) was measured by spectroscopic ellipsometry (SE, J.A.Woollam Co.).

3. Results and discussion

Figure 1 shows Raman spectra of BaSi₂ with and without a-Si:H capping layer annealed at different annealing temperature. Here, samples are denoted as BaSi₂- $d_{a-Si:H}/T_a$, e.g., BaSi₂-10/700 ($d_{a-Si:H}$ = 10 nm and T_a = 700 °C). Typically, there are five Raman bands corresponding to the vibration of the [Si₄]⁴⁻ cluster in BaSi₂, which are assigned to three vibrational modes, namely, E (~276 cm⁻¹ and ~293 cm⁻¹), F₂ (~355 cm⁻¹ and ~376 cm⁻¹), and A₁ (~486 cm⁻¹) [1]. Those Raman peaks can be observed with all samples. It indicates the crystallization of BaSi₂ after high-temperature annealing. Besides five BaSi₂ peaks, Si peaks at ~520 cm⁻¹ can also be noticed once annealing temperature is higher than 600 °C.

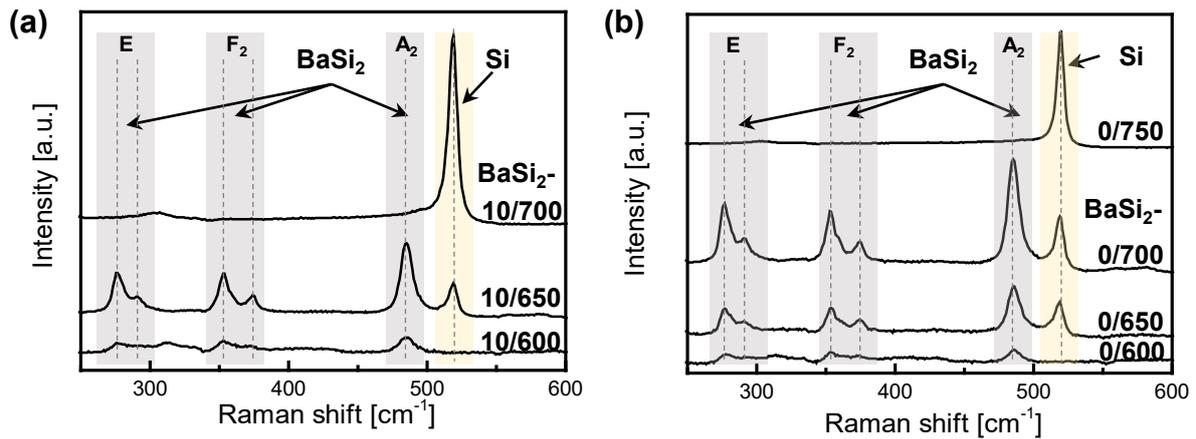


Figure 1. Raman spectra of (a) BaSi₂ capped with 10-nm a-Si:H and (b) without capping layer.

The existence of 10-nm a-Si:H makes no difference to shapes of Raman spectra in the case of $T_a \leq 650$ °C. By increasing T_a up to 700 °C, BaSi₂-10/700 only presents a Si peak, while BaSi₂ peaks are still there in BaSi₂-0/700. Further enhancing T_a to 750 °C can make BaSi₂-0/750 hold a similar Raman spectrum of BaSi₂-10/700. According to our previous research, the formation of Si peak (Si nanocrystal) is resulted from surface oxidation which leads Si atom isolation and further crystallization [7]. Based on Raman spectra observations, a-Si:H capping layers can in some degree enhance the Si isolation and crystallization.

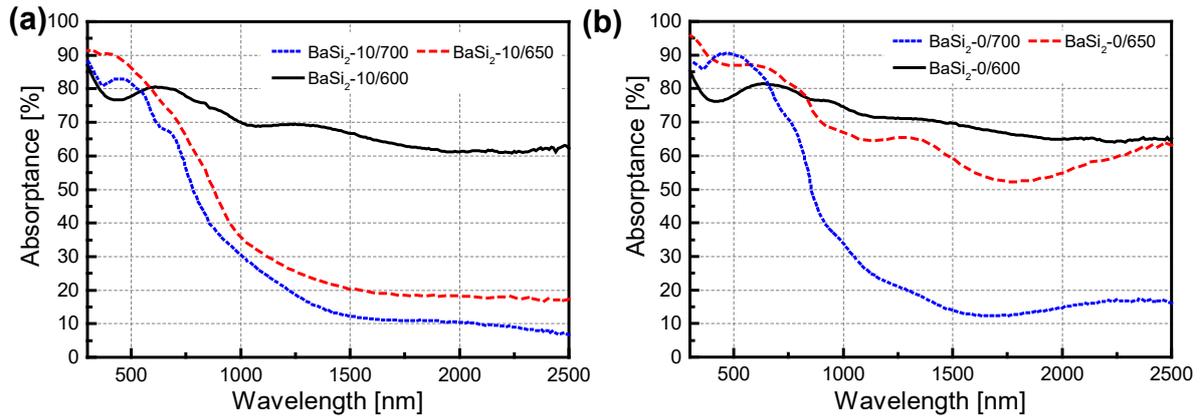


Figure 2. Absorbance of (a) BaSi₂ capped with 10-nm a-Si:H and (b) BaSi₂ without capping layer. Absorbance was calculated by 100% – reflectance – transmittance.

The similar trend can also be observed with optical properties. Absorbance curves are presented in Figure 2. Samples capped with 10-nm thick a-Si:H exhibit similar absorbance to samples annealed at higher temperature. For instance, sample BaSi₂-10/650 holds absorbance that is similar to that of the BaSi₂-0/700. The higher annealing temperature can enhance the crystallization of BaSi₂ and reduce the metallic and/or defective phases. Such improvement of crystalline quality decreases the absorbance in the long-wavelength range. The existence of a-Si:H layer hence may also suppress formation of defective and/or metallic phase within BaSi₂ films.

Figure 3 displays surface morphologies of BaSi₂ with and without a-Si:H capping layer (annealed at 650 °C). It is obvious that sample BaSi₂-10/650 exhibits a rougher surface structure with a surface roughness (σ_{RMS}) of 47 nm (twice higher than that of bare BaSi₂ film 20 nm).

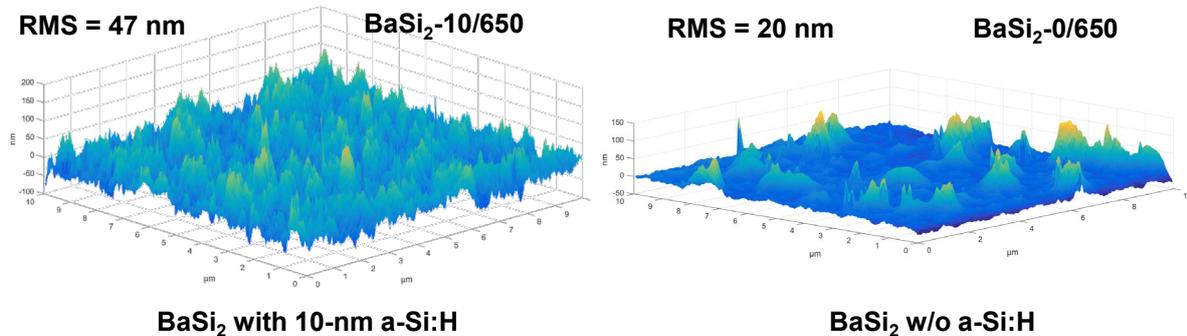


Figure 3. AFM images of BaSi₂ surfaces with and without a-Si:H capping layer after being annealed at 650 °C

Figure 4 presents samples with different a-Si:H thicknesses ranging from 0 to 50 nm. BaSi₂ film without a-Si:H exhibits a high absorbance in the long-wavelength range (> 1000 nm). Applying a-Si:H capping layer can effectively decrease the absorbance in the long-wavelength range. Sample BaSi₂-10/650 displays the lowest absorbance (~18%). On the other hand, BaSi₂-50/650 and -20/650 present similar absorbance around 40%, which is closer to that of BaSi₂-0/650. Still, BaSi₂-50/650 and BaSi₂-20/650 exhibit better crystalline quality according to the decrease of absorbance.

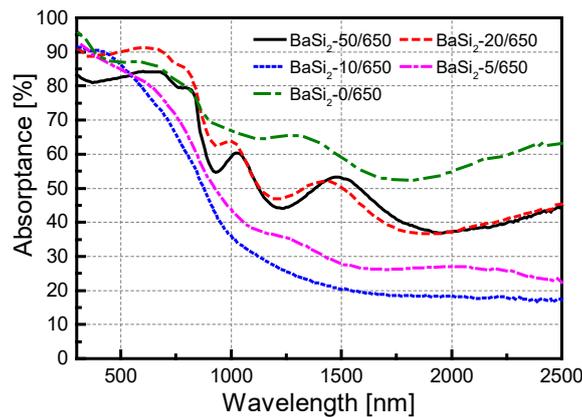
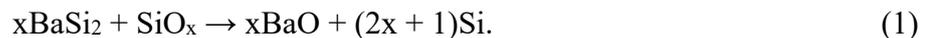


Figure 4. Absorptance of BaSi₂ with different a-Si:H capping layer thickness.

According to above results, effects of a-Si:H on BaSi₂ film qualities are mainly related to two processes, i.e., surface oxidation and bulk crystallization. During the high temperature annealing treatment, the a-Si:H capping layer also suffers the issue of oxidation. The outcome of a-Si:H is mainly SiO_x, which in turn can react with BaSi₂ as in following reaction [7]:



In the case of thinner capping layer, such as 10 and 5 nm, the a-Si:H can be totally oxidized during annealing. The formed SiO_x further reacts with BaSi₂ in the surface and results in formation of an oxide layer containing Si nanocrystals. The existence of such oxide layer increases the Si peak intensity in Raman spectra and decreases concentrations of metallic and/or defective phase in the film. Hence, samples capped by 10-nm a-Si:H needs lower annealing temperature to achieve the similar performances (Raman spectra and optical properties) with bare BaSi₂ films. Such reaction also leads to an increase of surface roughness. In the case of thicker capping layer, only surface region of a-Si:H is oxidized. Buried region together with BaSi₂ can survive during annealing. Hence, BaSi₂-50/650 presents similar properties to BaSi₂-0/650 rather than BaSi₂-0/700.

Single thin a-Si:H layer (≤ 10 nm) cannot sufficiently prevent surface oxidation of BaSi₂ film during high-temperature annealing. The SiO_x formed by a-Si:H oxidation in turn accelerates the Ba diffusion. Thicker a-Si layer or multi-materials layer such as a-Si/SiO_x can be regarded as possible strategies to avoid high temperature surface oxidation of BaSi₂.

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