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Effects of Amorphous Si Capping Layer on Sputtered $BaSi_2$ Film Properties

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Regarded as a promising absorber material for solar cell applications, Barium disilicide ($BaSi_2$) 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 $BaSi_2$ 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 $BaSi_2$.

1. Introduction

Barium disilicide ($BaSi_2$) has been regarded as a promising light-absorbing material for high-performance thin-film solar cells [1]. The semiconducting $BaSi_2$ is orthorhombic and stable in the ambient condition [2], exhibits an unintentionally n-type conductivity [3], and possesses a suitable band gap (E_g = ~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 µs) [5], and essentially elemental abundance and non-toxicity. Theoretically, the attainable conversion efficiency (η) of $BaSi_2$ homojunction solar cells is up to 25% [6]. However, $BaSi_2$ 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 $BaSi_2$. Amorphous Si (a-Si) capping layer has been applied to suppress surface oxidation of $BaSi_2$ 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 $BaSi_2$ thin films. Property comparisons between a-Si:H/$BaSi_2$ structure and bare $BaSi_2$ 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 $BaSi_2$ target was deployed for the deposition of $BaSi_2$ films. Prior to the growth, a pre-sputtering process was carried out for 10 min. $BaSi_2$ 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-depended 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 ($d_{a\text{-}Si;H}$) was measured by spectroscopic ellipsometry (SE, J.A.Woollam Co.).

3. Results and discussion

Figure 1 shows Raman spectra of $BaSi_2$ with and without a-Si:H capping layer annealed at different annealing temperature. Here, samples are denoted as $BaSi_2$-$d_{a\text{-}Si;H}$/T_a, e.g., $BaSi_2$-10/700 ($d_{a\text{-}Si;H}$ = 10 nm and T_a = 700 °C). Typically, there are five Raman bands corresponding to the vibration of the $[Si_4]^{4-}$ cluster in $BaSi_2$, which are assigned to three vibrational modes, namely, E (~276 cm^{-1} and ~293 cm^{-1}), F_2 (~355 cm^{-1} and ~376 cm^{-1}), and A_1 (~486 cm−1) [1]. Those Raman peaks can be observed with all samples. It indicates the crystallization of $BaSi_2$ after high-temperature annealing. Besides five $BaSi_2$ peaks, Si peaks at ~520 cm^{-1} can also be noticed once annealing temperature is higher than 600 °C.

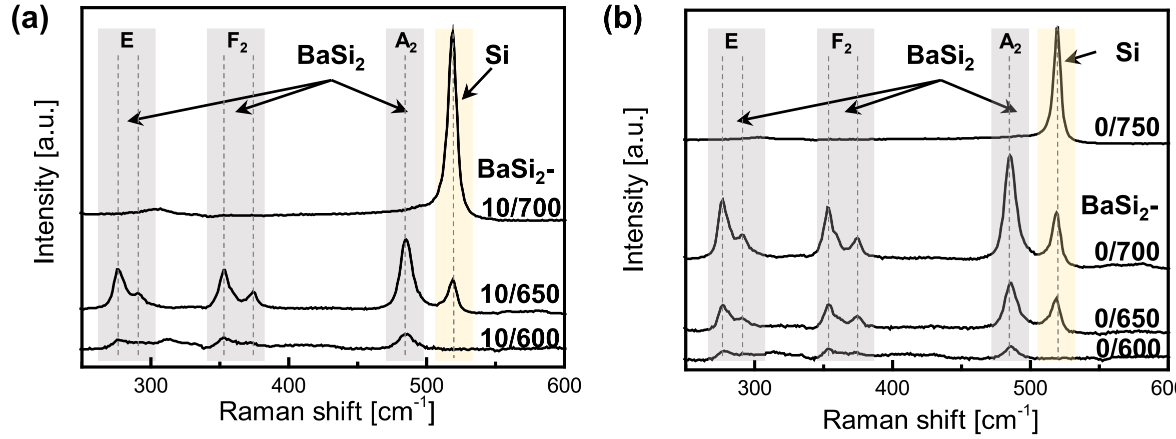

Figure 1. Raman spectra of (a) $BaSi_2$ capped with 10-nm a-Si:H and (b) without capping layer.

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, $BaSi_2$-10/700 only presents a Si peak, while $BaSi_2$ peaks are still there in $BaSi_2$-0/700. Further enhancing T_a to 750 °C can make $BaSi_2$-0/750 hold a similar Raman spectrum of $BaSi_2$-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.

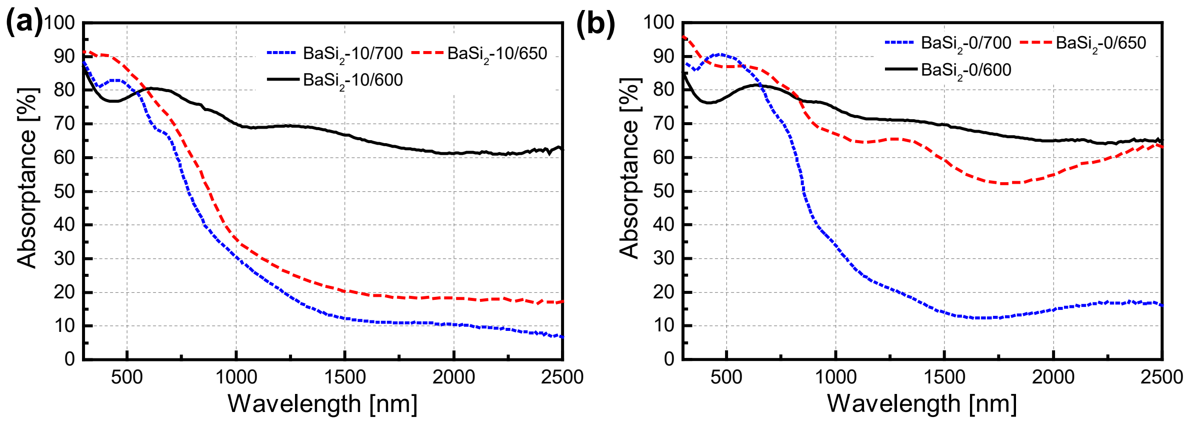

Figure 2. Absorptance of (a) $BaSi_2$ capped with 10-nm a-Si:H and (b) $BaSi_2$ without capping layer. Absorptance was calculated by 100% − reflectance – transmittance.

The similar trend can also be observed with optical properties. Absorptance curves are presented in Figure 2. Samples capped with 10-nm thick a-Si:H exhibit similar absorptance to samples annealed at higher temperature. For instance, sample $BaSi_2$-10/650 holds absorptance that is similar to that of the $BaSi_2$-0/700. The higher annealing temperature can enhance the crystallization of $BaSi_2$ and reduce the metallic and/or defective phases. Such improvement of crystalline quality decreases the absorptance in the long-wavelength range. The existence of a-Si:H layer hence may also suppress formation of defective and/or metallic phase within $BaSi_2$ films.

Figure 3 displays surface morphologies of $BaSi_2$ with and without a-Si:H capping layer (annealed at 650 °C). It is obvious that sample $BaSi_2$-10/650 exhibits a rougher surface structure with a surface roughness (σ_{RMS}) of 47 nm (twice higher than that of bare $BaSi_2$ film 20 nm).

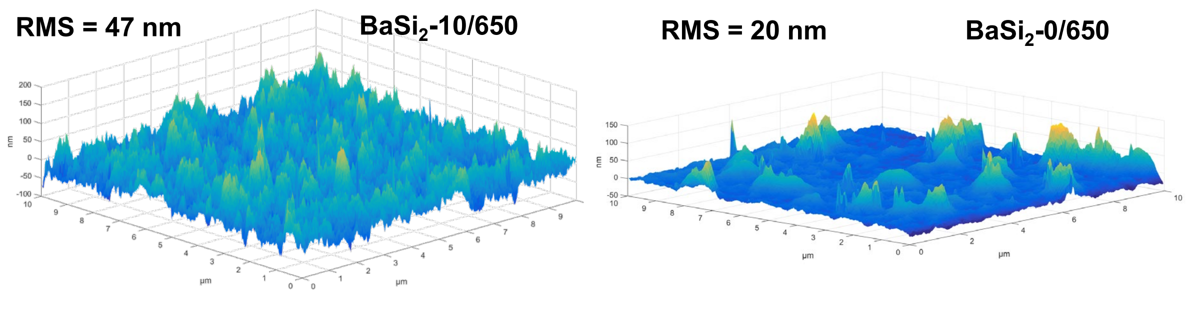

Figure 3. AFM images of $BaSi_2$ surfaces with and without a-Si:H capping layer after being annealed at 650 °C

Figure 4 presents samples with different a-Si:H thicknesses ranging from 0 to 50 nm. $BaSi_2$ film without a-Si:H exhibits a high absorptance in the long-wavelength range (> 1000 nm). Applying a-Si:H capping layer can effectively decrease the absorptance in the long-wavelength range. Sample $BaSi_2$-10/650 displays the lowest absorptance (~18%). On the other hand, $BaSi_2$-50/650 and -20/650 present similar absorptance around 40%, which is closer to that of $BaSi_2$-0/650. Still, $BaSi_2$-50/650 and $BaSi_2$-20/650 exhibit better crystalline quality according the decrease of absorptance.

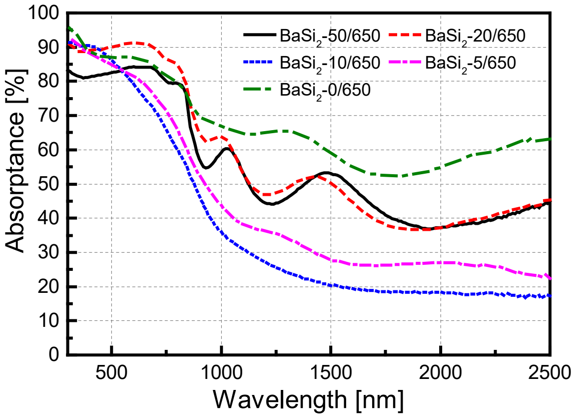

Figure 4. Absorptance of $BaSi_2$ with different a-Si:H capping layer thickness.

According to above results, effects of a-Si:H on $BaSi_2$ 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 $BaSi_2$ as in following reaction [7]:

$$xBaSi_2 + SiO_x \rightarrow xBaO + (2x + 1)Si. \quad (1)$$

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 $BaSi_2$ 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 $BaSi_2$ 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 $BaSi_2$ can survive during annealing. Hence, $BaSi_2$-50/650 presents similar properties to $BaSi_2$-0/650 rather than $BaSi_2$-0/700.

Single thin a-Si:H layer (≤ 10 nm) cannot sufficiently prevent surface oxidation of $BaSi_2$ 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 $BaSi_2$.

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