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Microstructural Characteristics of $BaSi_2$ Epitaxial Films Fabricated by Thermal Evaporation

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Abstract

Thermal evaporation is the most facile growth process of epitaxial films of $BaSi_2$, which is an emerging absorber-layer material for thin-film solar cells. In this study, we investigated the microstructure of $BaSi_2$ evaporated films to reveal the mechanism of epitaxial growth. Transmission electron microscopy analysis shows that the $BaSi_2$ film consists of three layers with different microstructural characteristics. The transfer of crystal orientation from the bottom to the top of the film is observed. The mechanism of epitaxial growth is discussed on the basis of the observed microstructure.

1. Introduction

The $BaSi_2$ semiconductor is an emerging absorber-layer material for thin-film solar cells, having suitable optical properties for photovoltaic applications such as a band gap of 1.3 eV and high absorption coefficients exceeding 10^4 cm^{-1} for photon energies over the band gap [1]. The abundance of constituent elements in the Earth's crust is also attractive for future large-scale deployment. In 2016, a power conversion efficiency of 9.9% was reported using a p-type $BaSi_2$ epitaxial film grown on n-type Si(111) substrate [2], which proved the availability of $BaSi_2$ for solar cells.

$BaSi_2$ epitaxial films are usually grown by molecular beam epitaxy on Si(111) and Si(100) substrates [3,4]. By more facile thermal-evaporation method using a $BaSi_2$ source, $BaSi_2$ epitaxial films can be formed on Si(100) substrates at a high substrate temperature of 700 ˚C [5]. It is important to understand the reason why epitaxial growth is possible at high temperatures by thermal evaporation for increased availability of $BaSi_2$ epitaxial films. The mechanism of the epitaxial growth of $BaSi_2$ by thermal evaporation is, however, still not clear. In this study, therefore, we have investigated the microstructure of the $BaSi_2$ evaporated films by transmission electron spectroscopy (TEM) to reveal the mechanism of epitaxial growth.

2. Experimental method

Commercial $BaSi_2$ lumps (99% in purity) were ground into granules and were used as evaporation source. The $BaSi_2$ source was melted on a tungsten boat by resistive heating and the vapor was deposited on Si(100) substrates heated at 700 °C. Before the deposition, the surface contaminant was removed by melting the source for 4 s. The obtained film was characterized by 2θ–ω X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM).

3. Results and discussion

Figure 1 shows the 2θ–ω XRD pattern of the $BaSi_2$ film fabricated by thermal evaporation. All observed peaks are attributed to the orthorhombic phase of $BaSi_2$ and Si. It is found that the $h00$ (h = 2, 4, 6) diffraction peaks are dominant among the $BaSi_2$ peaks, showing that the $BaSi_2$ evaporated films consist mainly of (100) oriented $BaSi_2$ crystal grains.

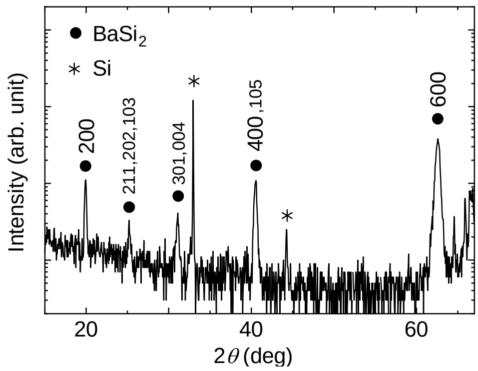

Fig. 1 2θ–ω XRD pattern of the $BaSi_2$ evaporated film deposited on Si(100) at a substrate temperature of 700 ˚C.

To reveal the microstructure of the $BaSi_2$ epitaxial film, the cross section was analyzed by TEM. Figure 2 shows the bright-field image of the $BaSi_2$ film. From the viewpoint of the grain size and shape, the $BaSi_2$ film can be divided into three layers. The first layer on the Si substrate consists of grains elongated toward the planar directions. It is also noticed that the interface between the Si substrate is wavy while that between the upper layer is flat, indicating that the first layer was formed through the diffusion of Ba atoms from the initially-deposited Ba-rich film into the Si substrate [6]. Here, $BaSi_2$ grains are probably formed holding the epitaxial relationship with the Si(100) substrate as $BaSi_2$[010]//Si[011] and $BaSi_2$[001]//Si[011] with $BaSi_2$(100)//Si(100) for two epitaxial variants [5]. The second layer formed on the first layer consists of smaller grains, probably because of a lot of crystal nuclei formed from the initially-deposited Ba-rich film. The third layer is comprised of larger grains than the second layer, which are elongated toward the growth direction. Since this layer is the thickest, the XRD pattern is presumably dominated by it. For the epitaxial growth of $BaSi_2$, therefore, it appears important for the orientation of the $BaSi_2$ grains have to be transferred to the third layer through the small-grained second layer.

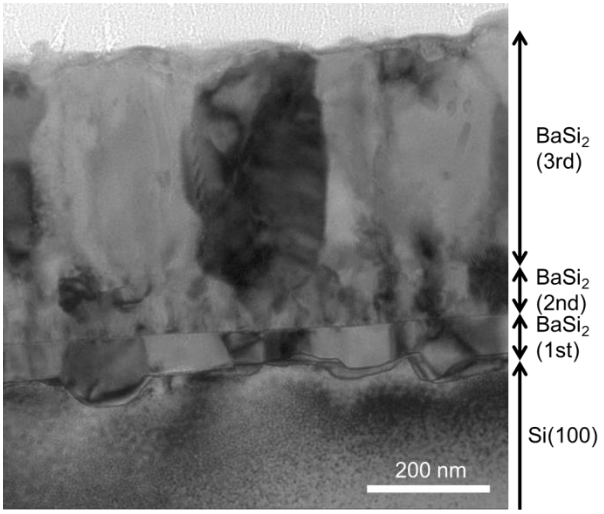

Fig. 2 Bright-field TEM image of the $BaSi_2$ evaporated film deposited at a substrate temperature of 700 ˚C.

Figure 3 displays the dark-field image of the same area as Fig. 2. It is confirmed that the orientation of some grains in the first layer is transferred up to the third layer. It is also clearly observed that the orientation of some grains in the first layer is not transferred to the second layer. For fabricating $BaSi_2$ epitaxial films by thermal evaporation, hence, the epitaxial growth at the interface between the first and second layers is important.

Since the composition of the vapor produced from $BaSi_2$ changes from Ba-rich to Si-rich as evaporation proceeds, the second layer is formed from the initially-deposited Ba-rich film through the out-diffusion of excess Ba atoms into the Si substrate and the upper layers. When substrate temperature is low, the Ba diffusion is suppressed and the upper layer may be deposited before $BaSi_2$ is formed in the second layer. In this case, the crystal orientation would not be transferred to the third layer. On the other hand, when substrate temperature is high enough, $BaSi_2$ is quickly formed in the second layer and some $BaSi_2$ grains have the same orientation as the bottom first layer so as to minimize the interface energy. In this case, the crystal orientation of the first layer can be transferred to the lately-deposited third layer, which can explain our observation of epitaxial growth at a high substrate temperature of 700 ˚C [5].

In short, initially-deposited Ba-rich part is the origin of the first and second layer while lately-deposited Si-rich part corresponds to the third layer. When the substrate temperature is high enough, Ba diffusion from the Ba-rich part into the substrate occurs rapidly and the $BaSi_2$ grains formed in the second layer can attain the epitaxial relationship with those of the first layer, which enables the epitaxial growth of the upper third layer. The proposed mechanism suggests the importance of the control of the second layer for controlling the microstructure of $BaSi_2$ evaporated films.

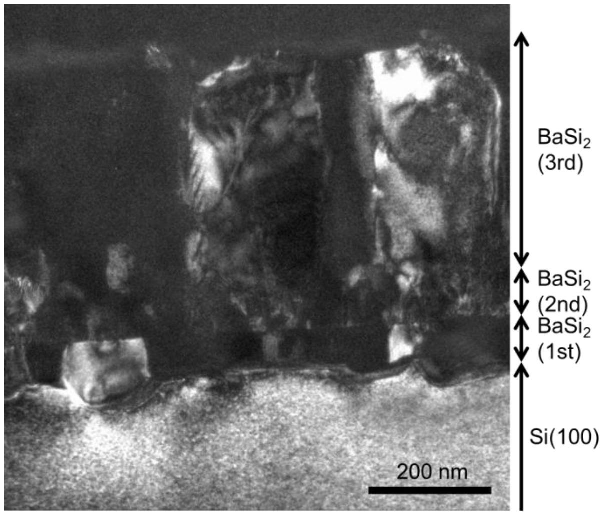

Fig. 3 Dark-field TEM image of the $BaSi_2$ evaporated film deposited at a substrate temperature of 700 ˚C.

4. Conclusions

The microstructure of the $BaSi_2$ epitaxial film fabricated by thermal evaporation has been investigated. It was found by TEM analysis that the $BaSi_2$ film consists of three layers having different microstructural characteristics. For the formation of epitaxial $BaSi_2$ grains up to the film surface, the epitaxial growth of the fine-grained second layer on the first layer seems to be most important.

Acknowledgements

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