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Structural and electrical characterizations of crack-free $BaSi_2$ thin films fabricated by thermal evaporation

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ABSTRACT

The $BaSi_2$ semiconductor is a promising candidate for an earth-abundant solar cell absorber. In this study, we have realized a crack-free $BaSi_2$ film by a simple thermal evaporation technique on a CaF_2 substrate at a growth temperature of 500 °C for electrical characterization. A Si layer preliminarily formed on the substrate by sputtering is a key to obtain stoichiometric $BaSi_2$ film. Detailed structural characterization of the evaporated films with different Si layer thicknesses by X-ray diffraction, scanning and transmission electron microscopy demonstrates that a crack-free 370-nm-thick $BaSi_2$ film is formed by consuming the Si layer. It is observed that the 90-nm-thick bottom part is microcrystalline and contains Ar atoms, which come from Si deposition atmosphere. The surface of the $BaSi_2$ layer is found to be covered by an amorphous Si layer due to Si-rich vapor at the last stage of evaporation. Electrical properties of the $BaSi_2$ film are revealed by Hall measurement and the electron density and mobility are found to be 6×10^{20} cm^{-3} and 0.04 $cm^2/V{\cdot}s$, respectively. Owing to a better crystalline quality contributed by the preliminarily-deposited Si layer, minority-carrier lifetime of the evaporated film (0.6 μs) is twenty times longer than previous films on glass substrates.

1. Introduction

In order to considerably suppress greenhouse gas emission by large-scale deployment of photovoltaic technology, high-efficiency solar cells with earth-abundant elements are necessary. Orthorhombic $BaSi_2$ is attracting much attention as a light absorbing material because of an appropriate indirect absorption edge (1.13–1.34 eV [1–3]) for single-junction solar cells and high optical absorption coefficients, reaching 3×10^4 cm^{-1} for a photon energy of 1.5 eV [3]. The abundance of constituent elements in the earth's crust is also preferable for large-scale production. The potential of this material for high efficiency devices has been demonstrated by long minority-carrier lifetime and diffusion length up to 11 μs [4] and approximately 10 μm [5], respectively.

$BaSi_2$ films can be grown by the molecular beam epitaxy (MBE) [6,7], radio-frequency sputtering [8,9], and vacuum evaporation techniques [10,11]. The MBE enables high-quality *a*-axis-oriented films on Si(111) and Si(100) substrates [6,7]. The long carrier lifetime and diffusion length mentioned above were measured on the epitaxial films. The sputtering deposition, which was developed for large-area and high-speed growth, realized 1-μm-thick polycrystalline films with optical properties comparable to the epitaxial film [9]. The evaporation technique is a simpler deposition method than the others. An air-stable $BaSi_2$ source can be used without any pretreatment, while the MBE uses a reactive Ba source and the sputtering method requires compacting the powder to make a target. It should also be noted that the deposition rate (300 nm/min) of the evaporation method is considerably higher than sputtering (30 nm/min [9]) and MBE (2 nm/min [12]).

Single-phase $BaSi_2$ films have been realized on Si and glass substrates at 500–600 °C by thermal evaporation [10,11], and it has been revealed that the evaporated films have suitable optical properties and carrier lifetime for thin-film solar cell applications [10]. We have also investigated the film growth mechanism and found that the vapor composition changes from Ba rich to Si rich during evaporation and is Ba rich on average. A high growth temperature is needed to eliminate the composition gradient and Ba rich part through diffusion [10,11]. Electrical properties, however, are still unknown due to cracking of the films on insulating glass substrates. The cracking is probably due to the mismatch of thermal expansion coefficients between $BaSi_2$ and glass substrates [10]. In this study, therefore, we have employed a CaF_2 substrate, which has a similar linear expansion coefficient ($19–20 \times 10^{-6}$ K^{-1} [13,14]) to $BaSi_2$ (17.4, 14.9, and 14.8×10^{-6} K^{-1} along the *a*, *b*, and *c* axes, respectively [15]). Since the vapor produced from the $BaSi_2$ source is Ba-rich in composition [10], Si

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atoms must be additionally supplied for the formation of stoichiometric $BaSi_2$. We therefore introduce a Si supply layer on the CaF_2 substrate. The purpose of the present study is to realize a crack-free $BaSi_2$ evaporated film, which is essential for electrical characterizations. It is demonstrated that the use of CaF_2 substrate is effective for preventing cracks and that the difference in the linear expansion coefficient is the primary cause of crack formation. The effects of the preliminarily-deposited Si layer on the crystalline quality of evaporated films are also discussed.

2. Experimental method

A Si layer was prepared by radio-frequency magnetron sputtering on a single-crystalline CaF_2 substrate (orientation not specified) at room temperature. We call this layer a Si supply layer hereafter. Commercial $BaSi_2$ source (99% in purity, Kojundo Chemical Lab.) was melted on a tungsten boat and the vapor was deposited on the CaF_2 substrates with Si supply layers heated at 500 °C. The main metallic impurities in the $BaSi_2$ source are Sr (0.5%), Ca (0.4%), and Al (0.01%). The Si supply layer is amorphous at both room temperature and 500 °C, which was confirmed by broad Raman bands peaked at 467–468 cm^{-1} (not shown). The details of the evaporation procedure are mentioned in our previous papers [10,11]. While fixing the evaporation amount, the effects of different initial Si thicknesses (t_{Si}) of 0, 129, and 230 nm were studied. The structure of films was characterized by grazing-incidence X-ray diffraction analysis (XRD, Bruker Discover D8) with Cu Kα radiation, scanning electron microscopy (SEM, JEOL JSM-7001FA), and transmission electron microscopy (TEM, FEI Tecnai Osiris). The physical properties of films were investigated by Hall measurement (TOYO ResiTest8308) with the van der Pauw method and microwave-detected photoconductivity decay (μ-PCD, KOBELCO LTA-1512EP) measurement. For Hall measurement, Al ohmic contacts were deposited on the surface by radio-frequency magnetron sputtering at room temperature. The excitation source of μ-PCD was a 5 ns laser pulse with a wavelength of 349 nm. The $BaSi_2$ source was also analyzed by powder XRD (Rigaku MultiFlex).

3. Results and discussion

Fig. 1 shows XRD patterns of the evaporated films. All peaks can be indexed to the orthorhombic $BaSi_2$ phase, indicating that the crystalline phase is only $BaSi_2$. Without a Si supply layer [Fig. 1(a)], however, the peak intensity is low and only three peaks are clearly observed. This is possibly because Ba-rich film without a Si layer reacted with air to form Ba oxide upon air exposure, leading to smaller $BaSi_2$ volume than the films with Si supply layers. With t_{Si} = 129 nm [Fig. 1(b)], several peaks show higher intensities than the theoretical pattern, while similar relative intensities to the theoretical pattern are observed for t_{Si} = 230 nm [Fig. 1(c)]. This result indicates that $BaSi_2$ film with t_{Si} = 129 nm has preferred orientation while that with 230 nm is randomly oriented. The diffraction indices are displayed in the figure for significantly stronger peaks than the theoretical one. Since $h0l$ ($h>l$) peaks are noticeable, the $BaSi_2$ crystals may be oriented around the a and c axes with t_{Si} = 129 nm. This preferred orientation is probably not due to the epitaxy on the CaF_2 substrate because a thin Si layer remained between $BaSi_2$ and CaF_2 substrate, as found from the TEM images shown later in Fig. 3. The templating effect of the Si supply layer is also not likely since the Si supply layer was amorphous, which was confirmed by Raman spectroscopy from both the front and rear surfaces after annealing at 500 °C for 4.5 h in the evaporation chamber without $BaSi_2$ evaporation. Although the reason of the preferred orientation is not clear, the films without crystalline impurities are formed with the present method.

The cross-section and plan-view SEM images of the evaporated films are shown in Fig. 2. Without a Si layer, the interface between the film and substrate is rough [Fig. 2(a)], suggesting that the film reacted with the substrate. On the other hand, with Si layers, flat interfaces are

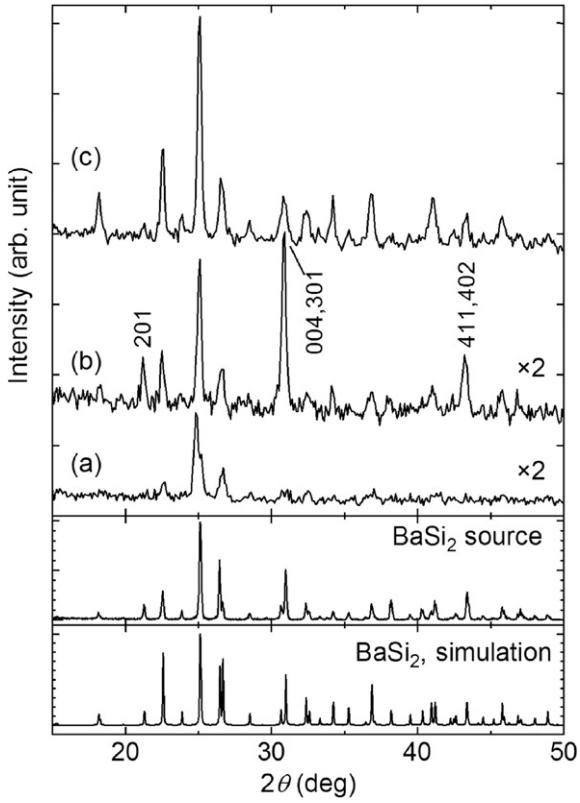

Fig. 1. XRD patterns of the evaporated films with (a) t_{Si} = 0, (b) 129, and (c) 230 nm. The X-ray incidence angle is 3.8°. Powder XRD pattern of the $BaSi_2$ source and a theoretical 2θ–θ pattern of randomly-oriented orthorhombic $BaSi_2$ phase are also displayed below the thin-film patterns.

observed. In particular, for t_{Si} = 230 nm, there is a 97-nm-thick dark layer exactly on the substrate. This dark layer is presumably a residual Si supply layer. That is, 230 − 97 = 133 nm of Si was consumed during the growth of 422 nm $BaSi_2$. A t_{Si} value of 129 nm was decided from this Si consumption rate so that the Si supply layer can be totally consumed. Such a dark layer, therefore, is not observed in Fig. 2(b).

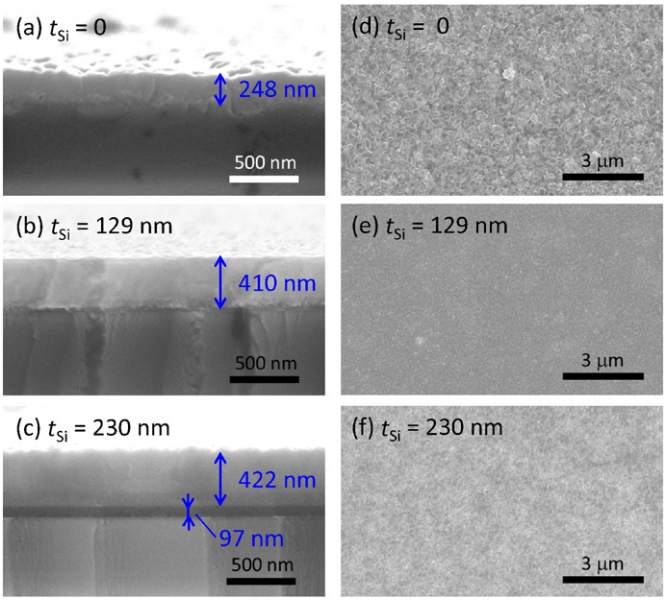

Fig. 2. (a)–(c) Cross-section and (d)–(f) plan-view SEM images of the evaporated films with (a, d) t_{Si} = 0, (b, e) 129, and (c, f) 230 nm.