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Oxidation-Induced Structure Transformation: Thin-Film Synthesis and Interface Investigations of Barium Disilicide toward Potential Photovoltaic Applications

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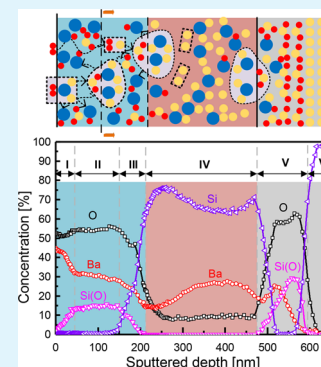
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S Supporting Information

ABSTRACT: Barium disilicide (BaSi_2) has been regarded as a promising absorber material for high-efficiency thin-film solar cells. However, it has confronted issues related to material synthesis and quality control. Here, we fabricate BaSi_2 thin films via an industrially applicable sputtering process and uncovered the mechanism of structure transformation. Polycrystalline BaSi_2 thin films are obtained through the sputtering process followed by a postannealing treatment. The crystalline quality and phase composition of sputtered BaSi_2 are characterized by Raman spectroscopy and X-ray diffraction (XRD). A higher annealing temperature can promote crystallization of BaSi_2 , but also causes an intensive surface oxidation and $\text{BaSi}_2/\text{SiO}_2$ interfacial diffusion. As a consequence, an inhomogeneous and layered structure of BaSi_2 is revealed by Auger electron spectroscopy (AES) and transmission electron microscopy (TEM). The thick oxide layer in such an inhomogeneous structure hinders further both optical and electrical characterizations of sputtered BaSi_2 . The structural transformation process of sputtered BaSi_2 films then is studied by the Raman depth-profiling method, and all of the above observations come to an oxidation-induced structure transformation mechanism. It interprets interfacial phenomena including surface oxidation and $\text{BaSi}_2/\text{SiO}_2$ interdiffusion, which lead to the inhomogeneous and layered structure of sputtered BaSi_2 . The mechanism can also be extended to epitaxial and evaporated BaSi_2 films. In addition, a glimpse toward future developments in both material and device levels is presented. Such fundamental knowledge on structural transformations and complex interfacial activities is significant for further quality control and interface engineering on BaSi_2 films toward high-efficiency solar cells.

KEYWORDS: barium disilicide, sputtering, annealing, structure transformation, interface, photovoltaic



INTRODUCTION

Sustainability, industrial ecology, and cost efficiency are regarded as key criteria guiding the development of the next-generation photovoltaic (PV) materials.^{1–4} Among a broad range of materials, the semiconducting barium disilicide (BaSi_2) has gained a renewed interest as a promising light-absorbing material toward high-performance thin-film PV devices.^{5,6} The semiconducting BaSi_2 is orthorhombic and can be ionically described as $2\text{Ba}^{2+}[\text{Si}_4]^{4-}$, in which the Si atom is covalently bonded with three neighboring Si atoms and forms the characteristic unit tetrahedron $[\text{Si}_4]^{4-}$.^{7,8} The orthorhombic BaSi_2 is stable in the ambient condition,⁹ exhibits an unintentionally n-type conductivity,¹⁰ and possesses a suitable band gap ($E_g = \sim 1.3$ eV) for solar energy conversion.^{11–14} In addition, its great potential also stems from 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,^{15,16} a long minority carrier lifetime τ (~ 10 – 27 μs),^{17–19} and essentially elemental abundance and

nontoxicity. Theoretically, the attainable conversion efficiency (η) of BaSi_2 homojunction solar cells is up to 25%.⁵ Despite the huge promise that BaSi_2 holds, the material is confronted with potential technological and scientific issues related to the material synthesis and quality control, which hinder further deployments of the material to cost-effective PV devices.

Low-cost synthesis routes of BaSi_2 come to the forefront. In fact, high-quality BaSi_2 films, which achieve an efficient solar cell device, have only been accomplished by the molecular beam epitaxy (MBE) technique.^{20,21} The distinct atomic-level film control advantage allows MBE a pioneering position in the high-quality material development. However, such an advantage always involves prohibitively expensive processes and the consequently high manufacturing cost, inhibiting the further practical applications. To this end, great efforts have been put

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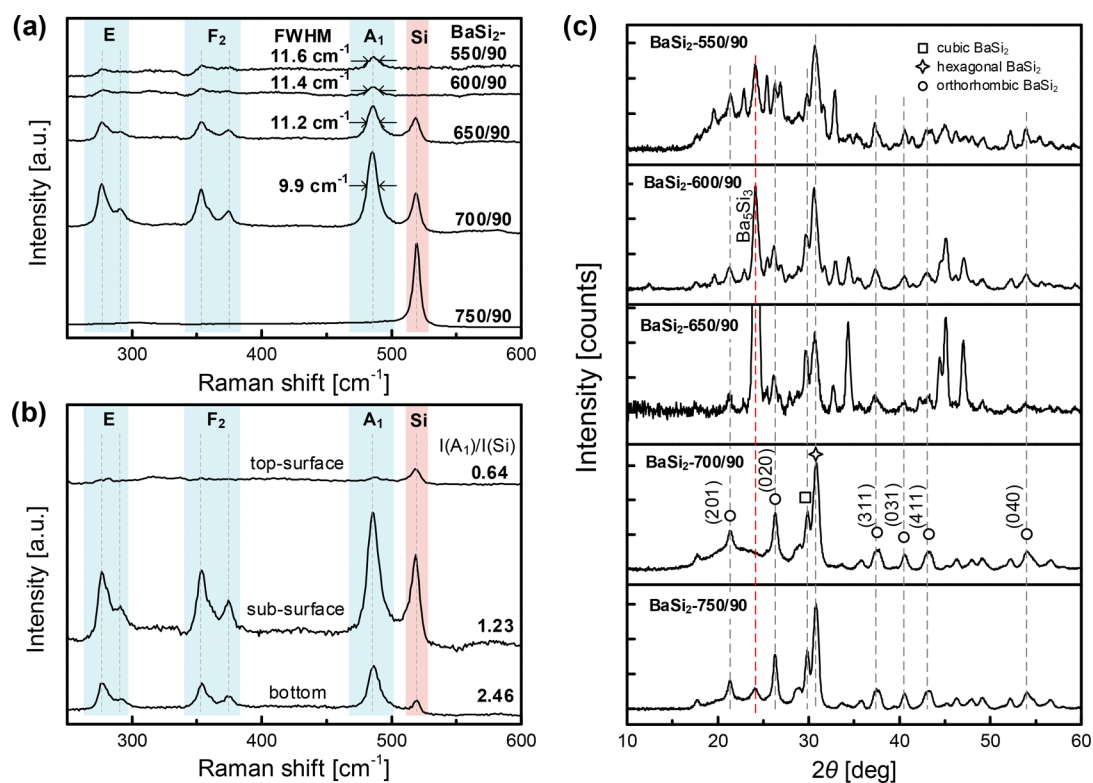


Figure 1. (a) Raman spectra of annealed BaSi₂ (collected from the film side). (b) Raman depth profile of the sample BaSi₂–650/90. (c) XRD patterns of annealed BaSi₂ films. All samples here are deposited on fused silica substrates.

into industrially applicable and commercially realistic processes for high-quality BaSi₂ fabrications. In addition to the chemical vapor deposition (CVD) technique,²² more attention is focused on alternative low-cost physical vapor deposition (PVD) approaches, such as thermal evaporation and sputtering.^{14,23–26} BaSi₂ thin films on various substrates with a high deposition rate up to 840 nm/min have been achieved via the thermal evaporation technique, presenting comparable quality to epitaxial films.^{14,25,27,28} Nevertheless, evaporation-source-related issues, including equilibrium vapor pressure difference and possible reactions with tungsten boat, increase difficulties in stoichiometry and further quality control of evaporated BaSi₂.⁶ In this regard, the sputtering technique, another feasible option for thin-film fabrications, is taken into consideration. In addition to the high deposition rate and elimination of ultrahigh vacuum (UHV) equipment, the sputtering process exhibits an excellent stoichiometry control for compound material depositions. However, limited knowledge on sputtered BaSi₂ films currently cannot support the further advancement from the material to practical PV devices.^{23,24,29,30} Fundamental research on synthesis and characterizations of sputtered BaSi₂ films still remain needed to be carried out.

The other crucial issue is the material quality control of BaSi₂ (especially at interfacial regions). The reactivity with oxygen and moisture does add difficulties to quality control at the air/BaSi₂ interface.^{6,31–33} The formed oxide layer consequently hinders the minority carrier (hole) transport with a barrier height of 3.9 eV.³³ The involved high-temperature conditions (Table S1) can further aggravate air/BaSi₂ interfacial oxidation. In addition to the air/BaSi₂ interface, the BaSi₂/solid (substrate) interface also experiences the atomic interdiffusion. Such interdiffusion alters the

stoichiometry, results in defective phases, and then degrades the film quality.^{10,34} In fact, those interfacial phenomena both at air/BaSi₂ and at BaSi₂/substrate interfaces increase difficulties on material quality control. Even though some approaches to avoiding deleterious interfacial activities have been put forward^{19,20,35} the concealed mechanisms of these interactions are still not well-documented, especially for the sputtering case. A better understanding of those interfacial activities is a key goal that helps in developing quality-optimization strategies^{31,36} and designing solar cell architectures.^{37,38}

Indeed, here we present a BaSi₂ thin-film synthesis route via an industrially applicable sputtering technique and reveal the structure transformation mechanism of BaSi₂ in a high-temperature process. Polycrystalline BaSi₂ thin films are obtained through the radio frequency (RF) sputtering process with a postannealing treatment. Higher annealing temperatures can enhance the crystallization of BaSi₂, but also induced an inhomogeneous and layered structure. Such a structure hinders further characterizations and applications of sputtered BaSi₂. Toward this, an oxidation-induced structure transformation mechanism is proposed on the basis of structural and interfacial observations and thermodynamic calculations. This knowledge regarding interfacial interactions and the structural transformation of BaSi₂ films serves as the foundation for future research on quality-control and interface-engineering strategies of BaSi₂ films toward solar cell applications.

RESULTS AND DISCUSSION

Synthesis and Characterizations of Sputtered BaSi₂ Thin Films. The sputtered BaSi₂ films on 10 × 10 cm² alkali-free glass presents a uniform thickness distribution with a target–substrate distance $d_{t-s} = 135$ mm (section S2,

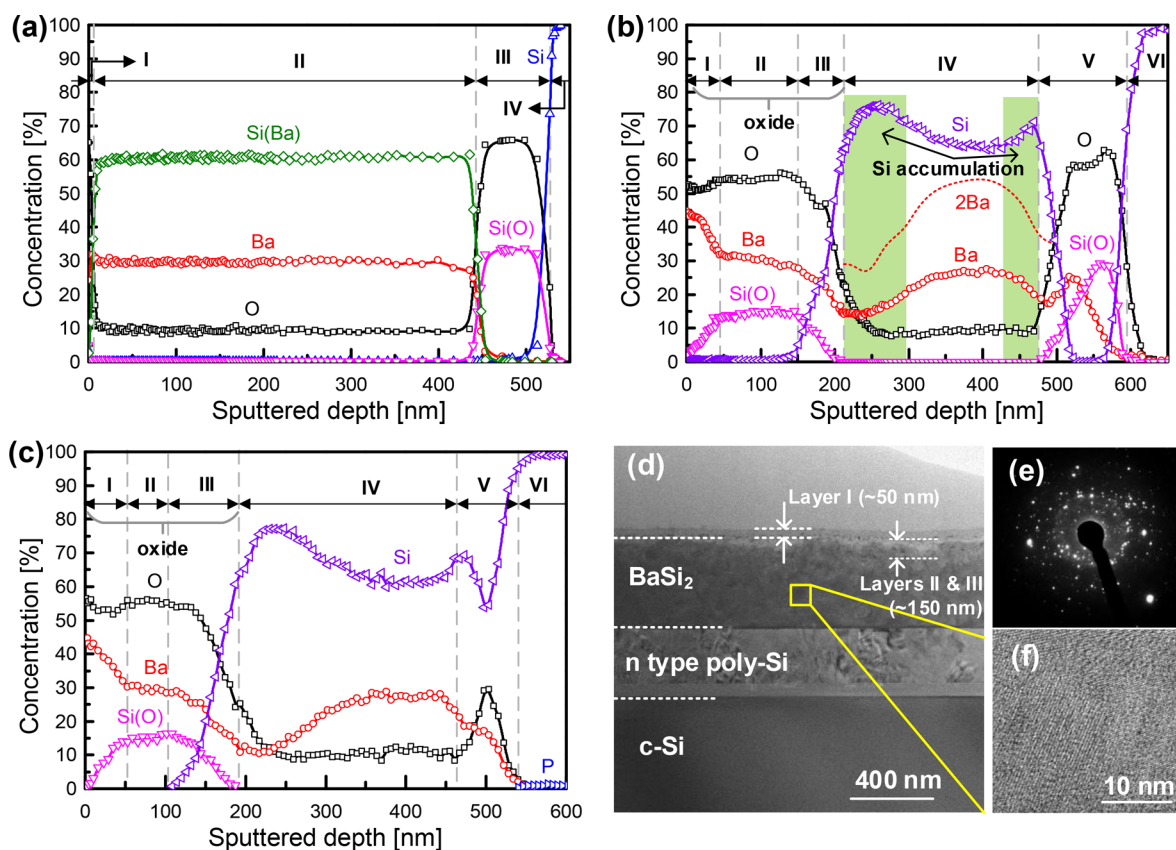


Figure 2. AES elemental concentration depth profiles of (a) $(\text{BaSi}_2\text{-RT}/0)/\text{SiO}_2/\text{c-Si}$, (b) $(\text{BaSi}_2\text{-650}/90)/\text{SiO}_2/\text{c-Si}$, and (c) $(\text{BaSi}_2\text{-650}/90)/\text{n-type poly-Si}/\text{c-Si}$. Si atoms bonded with Ba or O are marked as Si(Ba) and Si(O), respectively. It is hard to distinguish the metallic Si from that bonded with Ba in part b. (d) TEM cross-section image, (e) ED pattern, and (f) HR-TEM image of the $(\text{BaSi}_2\text{-650}/90)/\text{n-type poly-Si}/\text{c-Si}$ sample.

Supporting Information). The film growth rate is around 6.6 nm/min. However, the amorphous, instead of preferably crystalline, state of as-deposited BaSi_2 (Figure S2) prohibits its direct employment into practical thin-film solar cells. Thus, a subsequent thermal crystallization process was implemented. As-deposited samples were annealed at temperatures (T_a) ranging from 550 to 750 °C. Fused silica substrates here were utilized because of the high T_a . Annealing duration (t_a) was fixed at 90 min to ensure full crystallization. Here, samples are denoted as $\text{BaSi}_2\text{-}T_a/t_a$, e.g., $\text{BaSi}_2\text{-RT}/0$ (as-deposited), and $\text{BaSi}_2\text{-650}/90$ ($T_a = 650$ °C and $t_a = 90$ min).

Figure 1a shows the Raman spectra of annealed BaSi_2 films acquired by a 633 nm red laser. Typically, there are five Raman bands corresponding to the vibration of the $[\text{Si}_4]^{4-}$ 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}).^{39,40} As shown in Figure 1a, only $\text{BaSi}_2\text{-650}/90$ and $\text{BaSi}_2\text{-700}/90$ display sharper bands with fairly strong intensities, while bands of other samples annealed at lower T_a ($\text{BaSi}_2\text{-550}/90$ and $\text{BaSi}_2\text{-600}/90$) present less distinguishable vibration bands.

Full width at half-maximum (fwhm) values of the strongest-intensity A_1 band (~ 486 cm^{-1}) are calculated to quantitatively study the crystalline quality.^{28,41} A lower fwhm value refers to a better crystalline quality. As shown in Figure 1a, fwhm values decreased from 11.6 to 9.9 cm^{-1} by increasing T_a from 550 to 700 °C. This implies an enhancement of crystallization degree at higher T_a (but lower than 750 °C). Nevertheless, the higher T_a (≥ 650 °C), on the other hand, causes the formation of Si

nanocrystals (NCs), indicated by the band at ~ 519 cm^{-1} .^{42,43} Even worse is the sample $\text{BaSi}_2\text{-750}/90$, which only presents a Si NC band.

It should be emphasized that Raman spectroscopy only reflects the superficial structure information due to the limited laser penetration depth. For a deeper insight of sample structures, a Raman depth-profiling method is then established by applying both red (633 nm) and green (514 nm) lasers to measure from either the film or substrate side (section S4, Supporting Information). Accordingly, an inhomogeneous structure of $\text{BaSi}_2\text{-650}/90$ is portrayed by Figure 1b. An obvious change of Raman spectra, from surface to bottom, can be observed. Intensity ratios between A_1 and Si bands $I(A_1)/I(\text{Si})$ are calculated to roughly quantify concentration ratios between BaSi_2 and Si NCs within detected regions. Here, we see an increase of $I(A_1)/I(\text{Si})$ from 0.64 at the top-surface region to 2.46 at the buried bottom, implying a composition evolution. To be explicit, less BaSi_2 remains at the surface region, while Si NCs are inclined to form and accumulate at the surface.

Figure 1c presents the XRD patterns of annealed samples. Most of the strong diffraction peaks are related to orthorhombic BaSi_2 , which is consistent with the Raman spectroscopy and further confirms BaSi_2 crystallization. In addition to the orthorhombic phase, cubic and hexagonal BaSi_2 can also be observed. Cubic and hexagonal phases are reported to be metastable in ambient pressure, and form at high-temperature–pressure conditions (up to 1000 °C and 1 GPa).^{44–46} The existence of those phases may result from the

high energy of charged particles (Ba and Si) in the sputtering process. The existences of other low-concentration (less than 7% of the analyzed film) barium silicon compounds such as Ba_3Si_3 can also be noticed, the diffraction peak intensities of which decrease with the increase of T_a . Formation mechanisms of those phases and compositions remain to be uncovered for the goal of obtaining single-phase orthorhombic BaSi_2 .

It is worth noting that BaSi_2 diffraction peaks can also be observed in BaSi_2 -750/90, in which sample $[\text{Si}_4]^{4-}$ Raman vibrational bands cannot be collected from either the film or substrate side (Figure S4). This suggests the existence of a BaSi_2 layer that is sandwiched between two thick non- BaSi_2 layers in the BaSi_2 -750/90. The possible amorphous and/or microcrystalline state of non- BaSi_2 layers prohibits their being detected by XRD or Raman. Additionally, the absence of $[\text{Si}_4]^{4-}$ Raman bands indicates that the higher annealing is presumed to enhance the non- BaSi_2 layer growth.

Auger electron spectroscopy (AES) was then employed to determine the elemental composition and structure. Because of the requirement of conducting substrates for measurements, crystalline silicon (*c*-Si) wafers instead of fused silica substrates were utilized here. Prior to the BaSi_2 growth, *c*-Si substrates were coated with interlayers, including SiO_2 and p-, and n-type polycrystalline silicon (poly-Si).⁴⁷ Employments of the interlayer can avoid the influence of *c*-Si orientation on film growth, and make it possible to study the case of glass substrates.

Figure 2a displays the depth elemental concentrations of the as-deposited BaSi_2 film with a structure of $(\text{BaSi}_2\text{-RT}/0)/\text{SiO}_2/\text{c-Si}$. The layer structure is quite distinguishable, including the native oxide layer (Layer I, ca. 5 nm, Figure S7), the BaSi_2 (Layer II, ca. 450 nm), the SiO_2 interlayer (Layer III), and the *c*-Si substrate (Layer IV). A constant ratio of Ba:Si = 1:2 throughout the Layer II reflects the excellent stoichiometry control of the sputtering technique. In addition, no obvious interdiffusion phenomenon can be observed within the $\text{BaSi}_2\text{-RT}/0$.

However, the existence of 10% oxygen that uniformly distributes throughout the Layer II can also be observed. There are three potential sources of the oxygen, including oxygen diffusing from SiO_2 , the native oxidation, and the residual oxygen in the chamber. First, thermodynamic nonequilibrium states of atoms during the sputtering process can induce the oxygen diffusion at the $\text{BaSi}_2/\text{SiO}_2$ interface. On the other hand, the amorphous nature of the as-deposited film, containing a high density of defects and disorder structures, may enhance the chance for oxygen (in the air) bonding with Ba and Si during the sample storage. However, the absence of oxygen concentration gradient near $\text{BaSi}_2/\text{SiO}_2$ and air/ BaSi_2 interfaces suggests that oxygen is less likely to originate from the two above-discussed sources. Another possible source is the residual O_2 and moisture in the deposition chamber. Given that the base pressure of deposition chamber is around 2×10^{-4} Pa, the O_2 partial pressure, as a result, is in the order of 10^{-5} Pa. This ensures a sufficient number of oxygen atoms for incorporation in BaSi_2 films. Because of its incorporation with BaSi_2 during deposition, the oxygen here is denoted as internal O. Not only in the case of sputtering, similar oxygen incorporation phenomena have also been reported with epitaxial and evaporated BaSi_2 , which are executed at even lower pressures (on the order of 10^{-5} Pa).^{16,35,48} The existence of those internal O atoms does not alter the composition uniformity of sputtered BaSi_2 . Nevertheless, it is currently hard

to assert the effects of internal O on BaSi_2 properties, which needs further study.

Figure 2b shows the elemental structure of the BaSi_2 -650/90 on the same $\text{SiO}_2/\text{c-Si}$ substrate. BaSi_2 -650/90 exhibits an inhomogeneous structure in which a Si-rich BaSi_2 (Layer IV) is sandwiched between an oxide layer (Layers I–III) and an interdiffusion layer (interfacial region between Layers IV and V). Such a layered structure is consistent with Raman and XRD observations.

A high concentration of O at surface region is the outcome of intensive surface oxidation. We denote the O here as external O to distinguished from the O incorporating to BaSi_2 during the deposition. The oxide layer (holding a high O concentration) can be further divided into three sublayers illustrated in Figure 2b. Within the Layers I and II, only Si(O), Ba, and O can be detected, indicating the composition of SiO_2 and BaO. The concentration of SiO_2 increases throughout the Layer I, and eventually reaches a BaO: SiO_2 ratio of 2:1 (Layer II). Composition transition starts from the Layer III (near the oxide/ BaSi_2 interfacial region). Accompanied with the upward Si curve in the Layer III, both BaO and SiO_2 start to decrease while keeping BaO: SiO_2 = 2:1. The accumulation of Si in the Layer III results in the formation of Si NC (Figure 2b). Hence, the oxide layer (Layers I–III) presents a composition of BaO and SiO_2 , together with Si NCs. A higher annealing temperature, i.e., 750 °C, can promote the surface oxidation inducing a thicker oxide layer containing higher-concentration Si NCs. This explains the Raman spectrum of BaSi_2 -750/90 (Figure 1a), which only holds a Si NCs peak.

The phenomena of Si accumulation can also be observed on the other side of the “sandwich”, indicated in Figure 2b. This can be the consequence of the diffusion of Ba into the SiO_2 interlayer (Layer V). Ba unveils a relatively high diffusivity into SiO_2 and distributes throughout the Layer V. This accumulated Si also formed Si NCs, which is consistent with the Raman spectrum obtained from the substrate side (Figure 1c). Such Ba diffusion can be effectively suppressed by poly-Si interlayers. No Ba presents itself in the n-type poly-Si layer (Layer VI in Figure 2c). However, there is a relatively high concentration of O in the Layer V. The absence of Si(O) here implies that it is a Ba–Si–O complex oxide rather than a mixture of SiO_2 and BaO. O atoms here can also be the internal O, which may originate from the residual oxygen in the deposition chamber as well as O_2 and/or oxygen-containing groups adhering to the poly-Si surface. The case of p-type poly-Si (B-doped) is almost similar (Figure S7), except for the disappearance of B within the poly-Si interlayer (and/or B concentration is under detection limit).

The surface oxidation together with interfacial diffusion phenomena leave a Si-rich BaSi_2 layer in the center of the “sandwich”. As illustrated in the Figure 2b, Si atomic concentration is far more than twice that of Ba (2Ba curve), especially near the interfacial (oxide/ BaSi_2 and $\text{BaSi}_2/\text{SiO}_2$) regions. Not only the Si accumulations but also the Ba movement can be observed. Upon comparison of the overall Ba distribution in Figure 2a,b (also Figure 2c), the trend that Ba moves to the surface and substrate side after annealing is quite noticeable. Nevertheless, the internal oxygen still remains a constant concentration nearly 10% after annealing throughout the core region of the Layer IV (250–450 nm). This suggests a stable structure of O-incorporated BaSi_2 in high temperatures. In addition, it needs to be emphasized that it is external O (from annealing atmosphere and SiO_2 substrate)

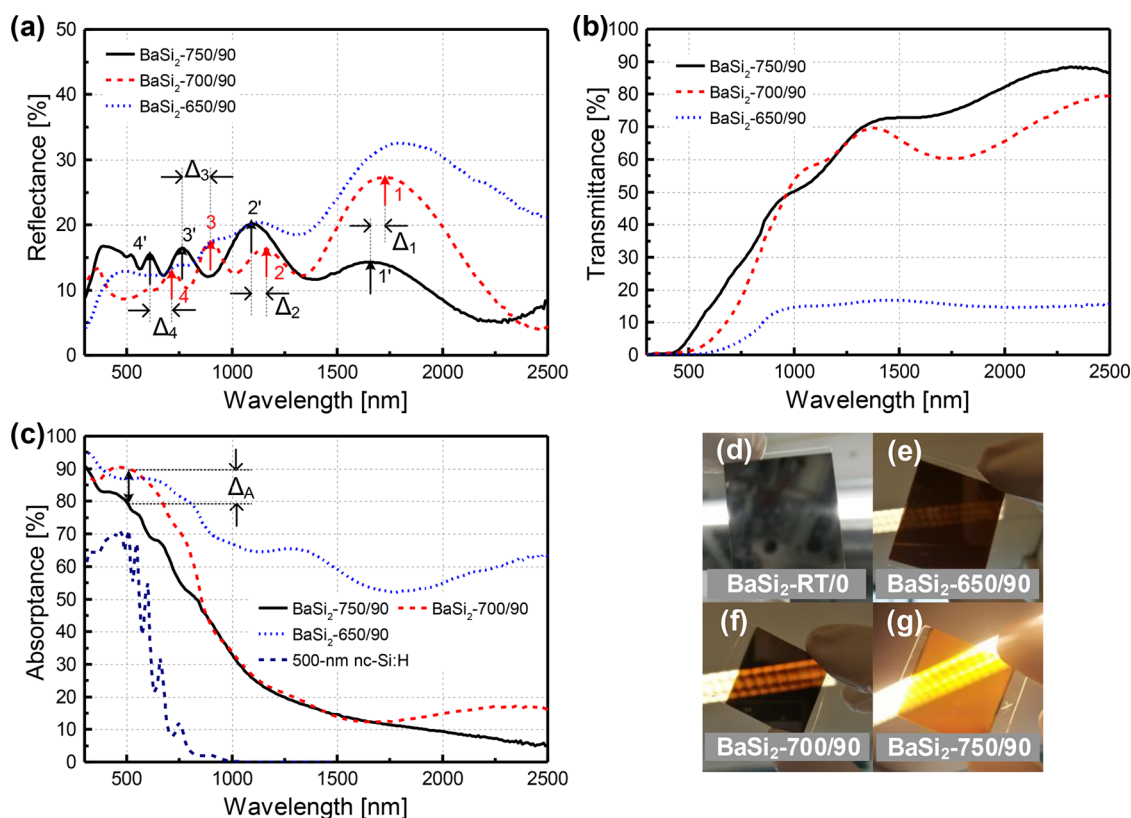


Figure 3. Wavelength-dependent (a) reflectance, (b) transmittance, and (c) absorbance curves of annealed BaSi_2 thin films. Interference peak position shifts, i.e., Δ_1 , Δ_2 , Δ_3 , and Δ_4 are indicated in part a. The absorbance was calculated as follows: absorbance (%) = 100 – reflectance (%) – transmittance (%). The simulated absorbance curve of 500 nm thick *nc*-Si:H film is presented as the reference. The absorbance difference between BaSi_2 -700/90 and BaSi_2 -750/90 (Δ_A) is illustrated in part c. Photo images of (d) BaSi_2 -RT/0, (e) BaSi_2 -650/90, (f) BaSi_2 -700/90, and (g) BaSi_2 -750/90.

rather than internal O (from residual air in the deposition chamber) that alters the composition uniformity of sputtered BaSi_2 . Further attempts to obtain uniform sputtered BaSi_2 should be focused on the antioxidation/diffusion layer development, and poly-Si (and/or *a*-Si) can be regarded as a potential candidate.

Another phenomenon that should not be neglected is the slight shift of the boundary between the Layers II and III (Figure 2b,c, and Figure S8), while the thickness of oxide layer keeps constant (~ 200 nm). The cross-section transmission electron microscopy (TEM) image in Figure 2d provides clues for the variation. The Layer I shows a relatively distinguishable and flat boundary with a thickness ~ 50 nm. However, Layers II and III almost merge together and are hard to be distinguished from the BaSi_2 layer. The variation in gray-scale near the oxide/ BaSi_2 interfacial region suggests the nonuniform composition and/or structure distribution in this region. Therefore, there is a high chance to collect AES depth profiles with different sublayer thicknesses. Additionally, the high-resolution TEM (HR-TEM) image of BaSi_2 bulk (Figure 2f) together with the electron diffraction (ED) pattern (Figure 2e) reveal the polycrystalline and multiphase structure of BaSi_2 -650/60.

Such a structure with a thick oxide layer prohibits material characterizations and the further application in PV solar cells. Figure 3a presents the wavelength-dependent reflectance curves of BaSi_2 -650/90, BaSi_2 -700/90, and BaSi_2 -750/90. Interference fringes in reflectance curves can result from the layered structure of high-temperature-annealed BaSi_2 films.

Interference peak position shifts with the increase of T_a can also be observed. This can be caused by the oxide layer growth (bulk BaSi_2 thickness decreasing) at higher T_a . In addition, increasing T_a from 650 to 700 °C leads to a drastic enhancement of the transmittance (Figure 3b). This can be interpreted by the improvement of BaSi_2 crystalline quality at higher T_a (Figure 1a) and/or oxide layer (SiO_2 and BaO) growth.

Figure 3c shows absorbance curves. BaSi_2 films exhibit high absorbance as compared to hydrogenated nanocrystalline silicon (*nc*-Si:H). However, metallic and/or defective phases (Figure 1b) induce an absorbance tail in the long wavelength range, and it can be attenuated by increasing T_a . BaSi_2 -700/90 and BaSi_2 -750/90 then present obvious absorption edges. However, higher T_a up to 750 °C in turn reduces the absorbance in the visible wavelength range. The absorbance difference between BaSi_2 -700/90 and BaSi_2 -750/90 reaches a maximum at a wavelength around 500 nm, which is near the absorbance peak of *nc*-Si:H (Figure 3c). Hence, such an absorbance difference can be a consequence of formations of a higher concentration of Si NCs and/or the thicker oxide layer at higher T_a . Those optical properties are also consistent with appearances of samples (Figure 3d–f), including the change of the transparency and brownish color (annealed samples).

Even though optical characterizations provide some information on annealed samples, it is hard to obtain the exact optical properties of bulk BaSi_2 with the existence of such a layered structure (oxide and Si NCs). The same goes for the

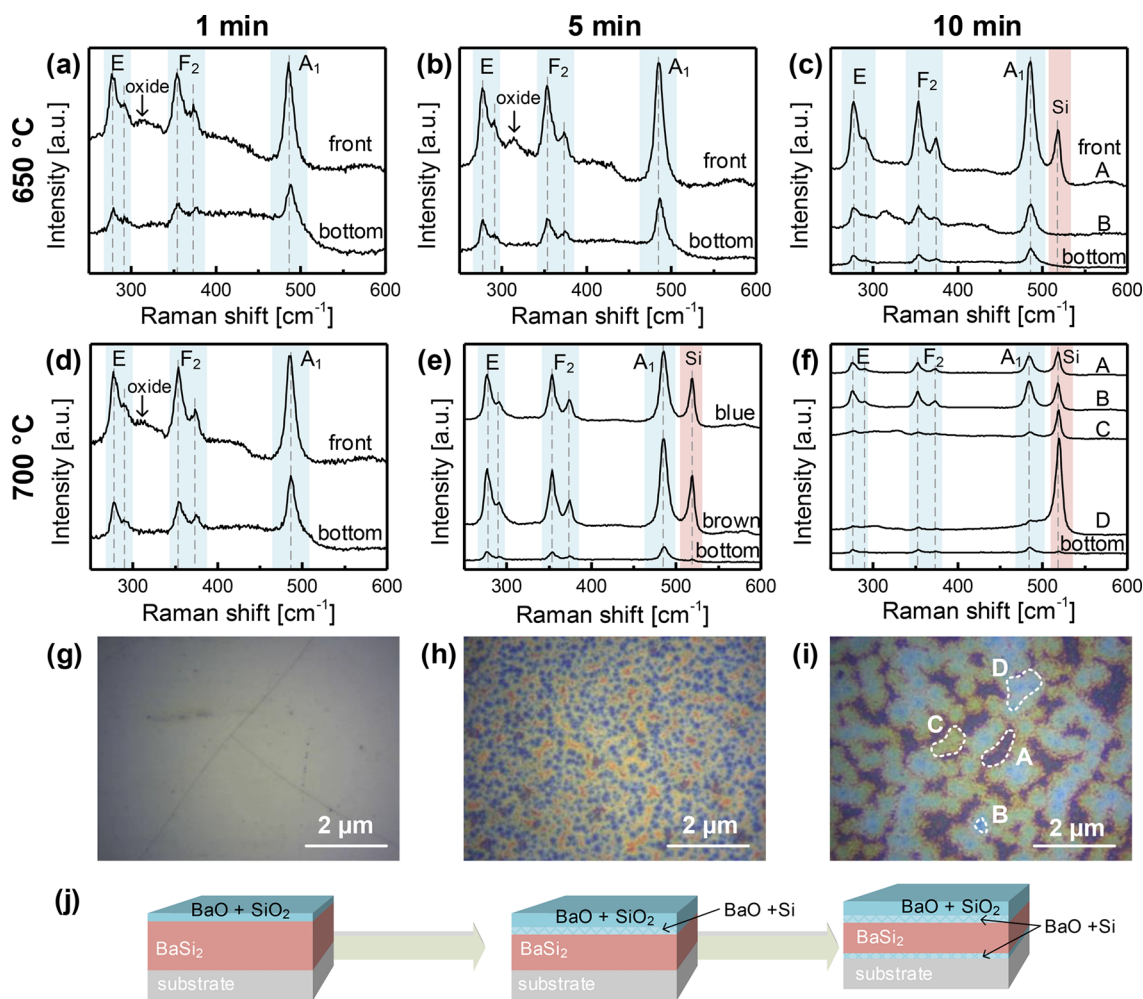


Figure 4. Raman spectra of (a) BaSi₂-650/1, (b) BaSi₂-650/5, (c) BaSi₂-650/10, (d) BaSi₂-700/1, (e) BaSi₂-700/5, and (f) BaSi₂-700/10. The vibrational band at ~315 cm⁻¹, indicated by arrows, refers to surface oxides. Optical microscope images of (g) BaSi₂-700/1, (h) BaSi₂-700/5, and (i) BaSi₂-700/10 were captured by the Raman setup. (j) Schematic representation of BaSi₂ structural evolution in the time scale.

electrical properties. The thick oxide layer at the front side inhibits proper measurement due to high contact resistance.

Investigation on Sputtered BaSi₂ Annealing Process.

A deeper understanding on the mechanism of the above-discussed structural transformation then is essential for sputtered BaSi₂ quality-optimization and further applications. Hence, the annealing process is temporally investigated by the established Raman depth-profiling method (only 633 nm laser is employed here). Raman depth profiles of BaSi₂-650/1, BaSi₂-650/5, and BaSi₂-650/10 are presented in Figure 4a–c, respectively. Vibration bands of [Si₄]⁴⁻ observed at all samples suggest the BaSi₂ crystallization. Prolonging the t_a sharpens the vibration bands, indicating the promotion of crystallization. It is additionally reflected by the decrease of absorbance (Figure S8c). The surface oxidation also happens, implicated by the oxide band ~315 cm⁻¹ (Figure 4a,b).⁴⁹ In addition, Raman spectra of some specific regions at the BaSi₂-650/10 surface present a Si band (Figure 4c and Figure S9).

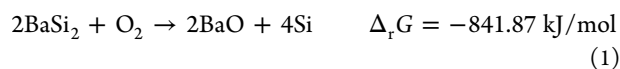
A more significant surface morphological change is observed with $T_a = 700$ °C (Figure 4g–i). Cracks at the sample BaSi₂-700/1, probably caused by the thermal expansion coefficient mismatch, disappear by prolonging the t_a . This can be the result of the surface composition variation, reflected by the surface color change (Figure 4g,h). However, we cannot assert

the situation of cracks below the surface region, which remains to be investigated.

Prolonging the t_a induces a nonuniform surface, including the appearance and composition. Accompanying the formation of blue and brown regions at the surface of BaSi₂-700/5, the Si Raman band can be noticed in the surface region (Figure 4e). However, the Si band in the bottom region is less distinguishable. Further extending the t_a to 10 min results in area expansions of blue and brown regions (Figure 4i). Moreover, some regions, i.e., C and D regions in Figure 4i, only exhibit strong Si bands in Raman spectra (Figure 4f). In addition, the Si band appears at the bottom of BaSi₂-700/10 (Figure S10).

Accordingly, the annealing process of BaSi₂, in respect to temporal structure and composition evolutions, can be roughly divided into three phases: (i) Si NC free and uniform surface oxidation, (ii) Si NC formation involving nonuniform surface oxidation, and (iii) Si NC formation in the bottom region, as illustrated by Figure 4j.

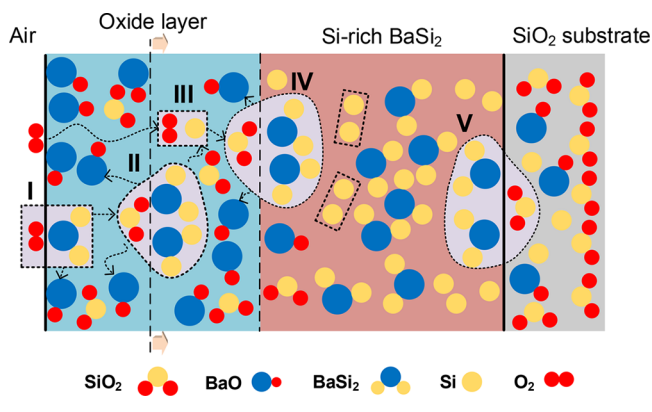
Oxidation-Induced Structure Transformation of BaSi₂. Previous research has credited the BaSi₂ oxidation and Si NC formation to the following reaction:



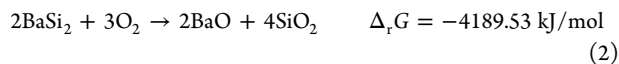
by which Si atoms (or $[\text{Si}_4]^{4-}$) are isolated and form Si NCs.^{49,50} $\Delta_r G$ is the change in Gibbs free energy of the reaction at the temperature of 650 °C (923 K). $\Delta_r G$ is calculated by the standard formation enthalpy and entropy of the reactant and resultant.³² The thermodynamic properties of BaSi_2 powder here are utilized.^{51,52}

Equation 1 can hardly explain the structural transformation of BaSi_2 in either the depth or time scale as described before. By such a single-stage reaction, Si NCs are supposed to distribute uniformly in the surface region, and should be formed in the initial oxidation phase. Herein, an oxidation-induced structure transformation mechanism is proposed and illustrated in Scheme 1, which is based on the above structure and interface investigations. The single-stage reaction (eq 1) is elaborated to a multistage variation including three major phases.

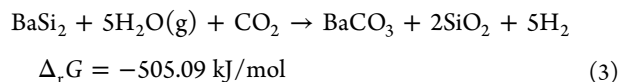
Scheme 1. Schematic Representation of Oxidation-Induced Structure Transformation of BaSi_2 Films during the High-Temperature Annealing Process (Note That the Diagram Does Not Represent the Real Microstructures of the Materials)



Initial Oxidation Phase at the Air/ BaSi_2 Interface. In this first-stage phase, the film surface is rapidly oxidized by the residual O_2 (as well as the moisture) in the N_2 annealing ambient environment (process I in Scheme 1).

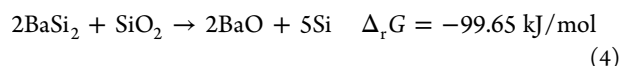


Consequently, the film surface is covered with a thin oxide layer, mainly consisting of BaO and SiO_2 . Additionally, the slight trace of C detected by AES (section S12, Supporting Information) in the surface can be regarded as the outcome of the reaction (not indicated in Scheme 1).



The crystallization process of BaSi_2 does initiate at the same time. Hence, BaSi_2 vibrational bands together with an oxide band can be found in Raman spectra of BaSi_2 -650/1, BaSi_2 -650/5, and BaSi_2 -700/1 (Figure 4a,b,d).

Oxide Layer Growth Phase at the Oxide/ BaSi_2 Interface. In addition to the surface oxidation, the resultant SiO_2 also provides an additional path for oxide/ BaSi_2 interfacial front advancing to the deeper region (process II in Scheme 1), which is defined as



Actually, it is also an oxidation reaction of BaSi_2 , due to the electron loss of Si in BaSi_2 . Indeed, the evolving oxide/ BaSi_2 interfacial front can be roughly tracked with simultaneous recording of depth Raman spectroscopy. Extending the annealing duration increases the concentration of isolated Si atoms. Those Si atoms can either form Si NCs, verified by the Si band in Raman spectra, or be oxidized to SiO_2 by the O_2 molecules that manage to penetrate through the thin oxide layer (process III in Scheme 1), reflected by the Si(O) curve upward trend in Layer I of Figure 2b,c.

More BaSi_2 is depleted by the process IV. Consequently, the oxide layer grows thicker, which inhibits the further penetration of O_2 as well as the subsequent formation of SiO_2 . This is the reason for the SiO_2 concentration decrease within the Layer III (Figure 2b,c). In this way, Si atoms (in the form of SiO_2) in the oxide layer are gradually yet only partially replaced by Ba atoms (forming BaO) from the buried BaSi_2 layer. Figuratively speaking, the Ba atoms are dragged to the upper oxide layer by the oxidation reactions. Hence, a higher concentration of Ba in the surface region is detected by AES spectroscopy (Figure 2b), while the Si atomic concentration can only reach nearly half of that of Ba. Note that the movement of Ba, in turn, leads to Si atom accumulation in the BaSi_2 layer, especially near the oxide/ BaSi_2 interface. Moreover, such SiO_2 -triggered oxide layer growth results in the boundary variation between Layers II and III (Figure 2b,c).

Oxygen-Driven Ba Diffusion at the $\text{BaSi}_2/\text{SiO}_2$ Interface. With a longer t_a , Si vibration bands appear in the Raman spectra in the case of detection from the substrate side. In such conditions, eq 4 is valid at the $\text{BaSi}_2/\text{SiO}_2$ interface. Similarly, isolated Si atoms formed Si NCs, interpreting the Si atom accumulation near the $\text{BaSi}_2/\text{SiO}_2$ interface (Figure 2b) as well as the consequent Ba diffusion into SiO_2 . In spite of the slight Ba diffusion within the thin oxide layer, no Ba atom can be detected throughout the n-type poly-Si interlayer in Figure 2c. Hence, we can assert that it is the oxygen (in SiO_2) that drives the Ba diffusion.

The oxidation-induced structure transformation mechanism allows interpretation of both composition and structure transitions of BaSi_2 thin films occurring at higher T_a , i.e., 650, 700, and 750 °C. However, cases of lower T_a , such as 550 and 600 °C, are more challenging to explain. Equations 1–4 can theoretically occur at $T_a = 550$ and 600 °C. Nevertheless, no distinguishable layered structure or Si NCs can be observed in samples BaSi_2 -550/90 and BaSi_2 -660/90 (Figures 1a and 2). This may result from the low-degree crystallization of BaSi_2 (Figure 1a) and the existence of impurities (Figure 1b). One can speculate that the BaSi_2 crystal structure transition from amorphous to crystalline state also changes the thermodynamic properties of the material. Those property changes may consequently suppress the above-mentioned structure transformation process. Further research remains to be conducted, which can lay an alternative path to enhance thermodynamic stability of BaSi_2 for a wider-processing-temperature PV application.

CONCLUSIONS

In summary, our work established an oxidation-induced structure transformation mechanism, based on structural and interfacial investigations on sputtered BaSi_2 films. Polycrystal-

line BaSi₂ thin films are obtained via RF sputtering followed by a postannealing process. An oxidation-induced structure transformation mechanism is proposed to interpret the transition from once homogeneous and stoichiometric films to a layered and multiphase structure. This is not limited to the sputtering case but can be extended to epitaxial and evaporated BaSi₂ thin films related to high-temperature processes. In addition, the established Raman spectroscopy depth-profiling method provides a fast and facile path for structural analysis of BaSi₂ films. Even though the sputtering technique is proven to be a suitable method for BaSi₂ thin-film synthesis, more efforts still need to be put on quality improvement of sputtered BaSi₂, especially on the development of antioxidation/diffusion approaches. This fundamental knowledge on structural transformations and complex interfacial activities is significant for further quality control and interface engineering on BaSi₂ films toward high-efficiency solar cells. With respect to device developments, interfacial phenomena discussed in this research also provide important information for a BaSi₂-based thin-film solar cell architecture design.

EXPERIMENTAL SECTION

Synthesis of BaSi₂ Thin Films. An RF magnetron sputtering setup (Kurt J. Lesker) was applied for the growth of BaSi₂ films. A stoichiometric ceramic BaSi₂ target (Tosoh) was installed. After the deposition chamber was pumped to less than 2×10^{-4} Pa, Ar gas flow was introduced into the chamber. The background pressure was maintained at 1 Pa during the whole growth process. Plasma power of 50 W was applied. Prior to the growth, a presputtering process was carried out for 10 min. The samples were deposited on either glass or silicon wafer substrates. After the sputtering process, the deposited BaSi₂ films were subsequently annealed for 90 min in a nitrogen atmosphere. Annealing temperatures ranged from 550 to 750 °C with a step of 50 °C.

Substrate Preparations. Glass and silicon wafer substrates were utilized in the research. Glass substrates including alkali-free (Corning EAGLE XG) glass and Heraeus Spectrosil 2000 fused silica were cleaned by ultrasonication in acetone and successively in isopropanol. SiO₂ and n- and p-type poly-Si interlayers were deposited on the c-Si substrate before the BaSi₂ growth. SiO₂ layers were formed by thermal oxidation with the wet method at 1050 °C. In terms of poly-Si, intrinsic a-Si layers were deposited in a Tempress low-pressure chemical vapor deposition (LP-CVD) tube furnace. Subsequently, P or B atoms were implanted into the a-Si layer by a Varian Implanter E500HP. Doped poly-Si layers were obtained by following high-temperature annealing at N₂ atmosphere.

Characterizations of BaSi₂ Thin Films. The thickness of the as-deposited sample was measured by the spectroscopic ellipsometry (SE, J.A.Woollam Co.). Raman spectra were acquired by an InVia Raman microscope (Renishaw) with excitation wavelengths of 514 and 633 nm. The XRD patterns were obtained by an automatic powder X-ray diffractometer X'Pert Pro equipped with an ultrafast linear semiconductor detector PIXcel and on a point proportional detector. Cu K α radiation ($\lambda = 0.154$ nm) was used as an X-ray source. The X-ray incidence angle ω was fixed at 0.5°. The wavelength-dependent reflectance and transmittance (R/T) were measured by a PerkinElmer Lambda 950 spectrometer. Elemental composition analysis was carried out in a Jeol JAMP 9510-F Auger microprobe at 10 keV energy with tilt angle of 30°. During sputtering cycles, 1000 eV Ar⁺ ions were utilized. The film cross-section images and ED patterns were acquired by a TEM (JEOL JEM-2200FS).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00486.

Detailed experimental methods, thickness distribution, Raman spectra, crystallite sizes, microscope images, and AES spectra (PDF)

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Notes

The authors declare no competing financial interest.

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