Mullite-Based Substrates for Polycrystalline Silicon Thin-Film Solar Cells

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薄膜型多結晶シリコンソーラーセル用ムライト基板

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The use of polycrystalline silicon thin-film on inexpensive ceramic substrates for solar cells is one of the most promising approaches to realize both their high performance and cost reduction. Mullite-based ceramics prepared from kaolin-alumina are appropriate for cost-effective substrates for the polycrystalline silicon thin-film solar cells. They fulfill requirements such as thermal and mechanical stability up to 1200°C and no thermal expansion mismatch with silicon.

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1. Introduction

Cost reduction for silicon solar cells can be accomplished in reduction of the amount of the expensive silicon and high efficiency in the processing. Polycrystalline silicon thin-film solar cells on inexpensive ceramic substrates are promising candidates for reducing costs.^{1)–4)} Preparation from inexpensive raw materials by conventional ceramic processing is one of the requirements for the development of the substrates. Refractoriness and thermal expansion coefficient matched to silicon are also required for the substrates, because high-temperature processing is utilized for high CVD deposition rates and heat treatment for recrystallization of deposited silicon.

Mullite is a crystalline oxide with a low thermal expansion coefficient, but which is a little larger than that of silicon. Mullite-based ceramics were developed using SiO_2 – Al_2O_3 powders containing 20–40 mass% Al_2O_3 synthesized by hydrolysis of metal alkoxide as the substrates which silicon chips were mounted on.⁵⁾ The thermal expansion coefficient of the ceramics at 30 to 400°C tended to increase with Al_2O_3 content. The optimum property was designed by adjusting $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the starting powders. Mullite ceramics can be also prepared from kaolin and alumina mixtures.^{6),7)} The use of inexpensive kaolin is preferable to more economical processing for the mullite-based substrates. New Zealand kaolin is a suitable candidate, because it is relatively pure compared with the other natural kaolin, and has not a large amount of alkali impurity which is detrimental to the mechanical property of the ceramics at high temperatures and leads to contamination during silicon layer deposition. However, the thermal expansion coefficients at high temperatures ($\sim 800^\circ\text{C}$) of mullite-based ceramics prepared from the kaolin and alumina has been not yet examined in detail.

In this study, mullite-based ceramics were prepared from New Zealand kaolin with a small amount of low-soda alumina. Compositional dependence of thermal expansion coefficient and flexural strength up to 1300°C of the ceramics were examined. The mullite-based ceramics were considered to be the most suitable candidate to serve as a substrate material, because they fulfilled most of the above requirements.

2. Experimental procedure

A New Zealand kaolin (Premium, mean grain size : 0.5

Table 1. Chemical Compositions of New Zealand Kaolin and Low-Soda Alumina (in mass%)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	Na_2O	K_2O	L.O.I
New Zealand Kaolin (Premium)	48.60	36.70	0.30	0.07	0.01	0.03	0.01	13.90
Low-soda Alumina (AES-12)	0.06	99.9	0.01	-----	-----	0.04	-----	0.1

(in mass%)

μm) supplied by Kyoritsu Ceramic Material Co., Japan and low-soda alumina (AES-12, mean grain size : 0.5 μm) from Sumitomo Chemical Co., Ltd., Japan were used. Their chemical compositions are listed in Table 1. The kaolin consisted of halloysite, cristobalite and quartz identified by X-ray diffraction (XRD) analysis.

The kaolin was first dehydrated by heating at 1000°C for 2 h. The dehydrated kaolin was mixed with the alumina using vibrational mill in methanol for 48 h. After drying, the mixed powder was passed through a 100 μm mesh sieve. The kaolin-alumina mixtures with 45–60 mass% Al_2O_3 were prepared as mentioned above. Powder compacts were formed by cold-isostatic pressing (CIP) at 240 MPa, and were sintered at 1550 to 1650°C for 2 h. In the firing process, the heating and cooling rate were 5 and 20°C/min, respectively. The phases present and the microstructure of sintered bodies were characterized by XRD and scanning electron microscopy (SEM). Bulk density of the sintered bodies was measured by the Archimedes' method using distilled water. Thermal expansion experiments were conducted from 25 to 800°C at a heating rate of 10°C/min in air, but for single crystal silicon in Ar. Three-point flexural strength was measured at room temperature to 1300°C on bars 3×3×30 mm, ground with a #400 diamond wheel, and chamfered with a #600 diamond disk. A span of 20 mm was used with a crosshead speed of 0.5 mm/min.

3. Results and discussion

Halloysite in the kaolin was dehydrated at 450–550°C during heating. Cristobalite and quartz were identified in the kaolin as crystalline phases by XRD after calcination at 1000°C. Mullite is first detected by XRD in the kaolin heated at 1250°C. The bodies sintered at 1600 or 1650°C were composed of elongated mullite grains and a glass containing impurities as an intergranular phase. On the other

hand, cristobalite remained in the bodies sintered at 1550°C as crystalline phases in addition to mullite. The bodies sintered at 1550°C are unsuitable for the substrate of thin-film polycrystalline silicon solar cell, because large volume change occurred at around 200°C in the bodies due to the α - β transformation of cristobalite. The surface roughness of the bodies sintered at 1650°C was higher than the bodies sintered at 1600°C. Therefore, the body sintered at 1600°C for 2 h was primarily characterized in this study.

The body sintered at 1600°C for 2 h (NZK16) had a coefficient of thermal expansion (CTE) of $3.48 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. It was slightly small, compared with that of silicon ($3.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$). The CTE of single-phase mullite ceramic with 73 mass% Al_2O_3 content sintered at 1600°C for 4 h was measured. The mullite ceramic was prepared from an alkoxide-derived powder with a purity of 99.99% (Hokko Chemical Industry Co., Ltd.). The CTE of the single-phase mullite ceramic was $5.12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, which was more than that of NZK16. Therefore, it is necessary to increase the content of mullite in the sintered body for a good match with the CTE of silicon. The formation of mullite is expected to increase with increasing the addition of alumina as inferred from SiO_2 - Al_2O_3 phase diagram.⁸⁾ A small amount of Al_2O_3 was added to the kaolin, and the samples with various Al_2O_3 contents were prepared. Figure 1 shows the effect of Al_2O_3 content on the CTE of the bodies sintered at 1600°C for 2 h. The CTE increased with Al_2O_3 content. The increase of mullite content resulted in the increase of the CTE. The CTE of the sintered body with 47 mass% Al_2O_3 (A47) was equivalent to that of silicon.

Figure 2 shows the SEM photographs of the polished surface and the chemical-etched surface of A47 sintered at 1600°C for 2 h. A47 consisted of elongated mullite grains with a size (minor axis) of less than 0.2–0.3 μm , as shown in Fig. 2(b), and an intergranular glassy phase. Residual pores with a size of 1–2 μm existed in the body (Fig. 2(a)). Bulk density and apparent porosity of A47 was 2.73 g/cm³ and 0.36%, respectively. Figure 3 shows temperature dependence of flexural strength of A47 sintered at 1600°C for 2 h. The strength kept steady up to 1000°C, and increased to a maximum at 1200°C, then fell drastically at 1300°C. This rise was attributed to softening of the intergranular glassy phase at the high temperatures.⁹⁾ The softening enabled the relaxation of stress concentration by blunting of crack tips. Plastic deformation also occurred at 1200°C.

Fig. 1. Thermal expansion coefficients (25–800°C) of the mullite-based ceramics as a function of Al_2O_3 content in the starting mixed powder (■ the specimen prepared from kaolin alone (NZK16), □ single-phase mullite ceramic).

Fig. 2. SEM photographs of the mullite-based ceramic with 47 mass% Al_2O_3 (A47) polished (a) and etched by 1% HF solution (b).

Fig. 3. Temperature dependence of flexural strength of the mullite-based ceramic with 47 mass% Al_2O_3 (A47).

However, the strength remained at the level of more than 400 MPa up to 1200°C.

4. Conclusions

These results prove the mullite-based ceramic (A47) prepared from New Zealand kaolin and low-soda alumina to be refractory enough to be used in the high-temperature process as a substrate for the polycrystalline silicon thin-film solar cells, and to occur no thermal expansion mismatch with silicon layer during heating and cooling.

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