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Investigation on a magnesiothermic reduction process for preparation of nanocrystalline silicon thin film

B. Ma, Z. Huang*, L. Mei, M. Fang, Y. Liu and X. Wu

Nanocrystalline silicon thin films were successfully prepared via a magnesiothermic reduction process. The initial magnesium content was restricted by the thickness of the film deposited on a quartz glass substrate by magnetron sputtering. After the magnesiothermic reduction process, the Raman spectroscopy results revealed a strong correlation between the thickness of the nanocrystalline thin films and the initial magnesium content. The thickness of the nanocrystalline thin films first increased to a maximum and then decreased as the initial magnesium content was further increased. Based on the solid-state reaction between Mg and SiO₂, the mechanism behind this phenomenon is explained. In addition, the Raman spectroscopy results showed that the average grain size was almost constant and the crystalline volume fraction was found to be proportional to the silicon content. The band gap of the nanocrystalline silicon thin film was estimated to be 2.94 eV.

Keywords: Nanocrystalline silicon film, Magnesiothermic reduction, Raman spectroscopy, Band gap

Introduction

Silicon-based thin-film materials are still widely applied in the electronics and photovoltaics industries, and in recent years, the research focus has shifted towards the development of nanostructured silicon thin-film materials. For instance, they can be used to produce thin-film transistors and solar cells. More specifically, in the electronics industry, the so-called ‘interconnect bottleneck’ problem has limited the achievable processor clock speed for many years. In order to solve this problem, such nanoscale silicon components have been implemented on a chip and successfully been tested. For photovoltaic applications, a higher optoelectronic performance is urgently required, which will benefit the next generation of high-efficiency thin-film Si solar cells. For this application, nanocrystalline silicon (nc-Si) thin films are the most promising candidate material. Owing to these great and promising application potential in thin-film semiconductor technologies, nc-Si thin films are becoming more and more important and more widely used in the optoelectronics, microelectronics and photovoltaics industry, especially in the field of photovoltaic solar cells.

Currently, the most widely used methods for the preparation of nc-Si thin films include the direct deposition of nc-Si and the re-crystallisation of a-Si thin films. However, both methods are associated with severe drawbacks. For instance, the re-crystallisation process requires an annealing treatment at temperatures above 1000°C, which strongly limits its application potential. In addition, the crystallite formation process is difficult to control when using this method. On the other hand, the direct deposition of nc-Si thin films requires the use of a dangerous and toxic gas (e.g., silane) as a precursor, which can result in environmental problems.

Previous studies have shown that magnesiothermic reduction with a nearly stoichiometric Mg/SiO₂ molar ratio is a convenient approach to convert different types of silicon dioxide into silicon. The reaction mechanism has also been elucidated in literature for a magnesium overdose, and it was demonstrated that a periodic layered structure consisting of alternating Mg₂Si and MgO-rich layers is formed in the SiO₂ zone in this case. Therefore, in order to avoid the occurrence of the alternating layered structure, the amount of magnesium must be strictly limited. Based on these results, an excellent work was recently reported by Wong et al., who fabricated nc-Si thin films via a magnesiothermic reduction at a relatively low temperature, and were able to adjust the silicon content (thickness) by varying the reaction time. However, the effect of the initial magnesium content on the silicon content (thickness), the crystalline volume fraction and the average grain size has not been studied so far. Furthermore, the mechanism governing the magnesiothermic reduction process has not been discussed.

In this study, we developed a process to prepare nc-Si thin films on a quartz glass substrate based on a magnesiothermic reduction reaction. By controlling the initial magnesium content (thickness of the deposited...
magnesium layer), the silicon content (i.e., the thickness of the produced nc-Si thin film), the crystalline volume fraction could be adjusted. Based on the theoretical explanations found in literature and our experimental data, we also established a model for the nc-Si thin-film formation mechanism. Finally, the band gap of the nc-Si thin film was estimated as well.

**Experimental**

First, magnesium thin films with different thicknesses (approx. 0.2, 0.4, 0.8, 1.2, and 1.6 µm) were deposited on quartz glass substrates using magnetron sputtering. Then, the magnesium-coated quartz glass substrates were placed in a tube furnace, and annealed at 550°C for 4 hours in a protective argon (99.999% purity) atmosphere. Finally, after the reaction, the quartz glass substrates were washed in a 1 M HCl solution and dried in a vacuum dryer.

The micro-morphology of the samples was investigated by scanning electron microscopy (SEM; ZEISS-MERLIN VP Compact microscope, Germany), and a micro-area chemical analysis was performed on the produced films using energy dispersive X-ray spectroscopy (EDS, INCA X-sight, Oxford Instruments, UK). Raman spectra were recorded using a Raman spectrometer (Horiba Jobin-Yvon LabRAM HR800, Horiba, Japan) equipped with a 633 nm He–Ne laser as excitation source. The optical properties of the samples were studied using a Diffuse Reflectance UV–Vis–NIR Spectrophotometer (Varian Cary 5000, now: Agilent Technologies, USA) with an integrated sphere attachment.

**Results and discussion**

**SEM and EDS analysis**

As shown in Fig. 1, magnesium films with different thickness (approx. 0.2, 0.4, 0.8, 1.2, and 1.6 µm) were obtained by magnetron sputtering. The presence of a small oxygen peak in the EDS spectrum (Fig. 1f) indicates that the films were slightly oxidised. A thin gold film was deposited on the samples prior to the measurements to improve their electrical conductivity, and make the images more clear. Therefore, a small Au peak is found in the EDS spectra.

After the magnesiothermic reduction process, the magnesium film (Fig. 1c) was found to be transformed into a double-layer film (Fig. 2a). The EDS analysis (Fig. 2b) revealed that the top layer is composed of three elements: Mg, Si, and O. However, after the washing process in the HCl solution, the top layer disappeared (Fig. 2c). Figure 2d confirms that the elemental magnesium has been removed. At such a relatively low reaction temperature (550°C), the compounds in the top layer (Fig. 2a) can only be MgO and Mg2Si (reactions (1) and (2)), and the top layer was found to be rich in MgO. In our experiments, the formation of a structure consisting of periodic layers as reported in literature was not observed, probably because we controlled the initial magnesium content, and it was much lower than in the experiments reported by Gutman et al. The low magnesium content limited the diffusion distance of magnesium and restricted further reaction. Figure 2d reveals an abundance of silicon and only small amounts of oxygen in the layer, which confirms the conversion of silicon dioxide to silicon. The oxidation may result from the washing process in the HCl solution.

**Raman analysis**

Raman spectroscopy is an effective analysis method and widely used to investigate silicon thin films, and therefore it was employed to study the structure of the prepared nc-Si films. For the sake of convenience, the fabricated samples were marked as T1–T5 corresponding to the thickness of the deposited magnesium films ranging from 200 nm to 1.6 µm. As shown in the inset image in Fig. 3a, the Raman spectrum of T3 features peaks characteristic for nc-Si thin films. More specifically, a typical single-crystalline silicon wafer shows a peak at around 520 cm⁻¹, which is a well-known optical phonon scattering peak. However, the peak obtained for the sample...
T3 is shifted to a lower wavenumber (≈515 cm\(^{-1}\)). In addition, the peak is asymmetrical compared to the peak of the wafer. These results confirm that sample T3 is a nc-Si film.

The other synthesised samples, i.e., T1, T2, T4 and T5, are identical in character to sample T3 (Fig. 3a). The amount of silicon produced in the thin film via the magnesiothermic reduction reaction (i.e., the film thickness) can be derived from the optical phonon scattering peak area (Fig. 3b), which was fitted by three Gaussian components: amorphous silicon, intermediate crystalline silicon and crystalline silicon (inset image in Fig. 3b).\(^{20}\) The results showed that the amount of silicon produced in the thin film (i.e., the film thickness) is not monotonically increasing with the initial magnesium content. A saturation point was obtained for sample T3, and then the film thickness was found to decrease as the magnesium content was further increased.

In order to explain this phenomenon, the solid-state reaction mechanism between Mg and SiO\(_2\) must be considered.\(^ {15-17}\) In the presence of a large amount of magnesium, with magnesium continually diffusing into the SiO\(_2\), a MgO-rich layer firstly forms at the interface, just underneath the magnesium film, and then a Mg\(_2\)Si-rich layer is produced below the MgO-rich layer. As the reaction continues, a periodic structure consisting of alternating MgO and Mg\(_2\)Si-rich layers is formed.

In contrast, in this study, the magnesium content (i.e., the nominal thickness of the deposited magnesium film) was much lower than in previous studies. However, by applying the solid-state reaction mechanism, a schematic model can also be deduced for this case (Fig. 4). When the magnesium content was below the saturation level, the magnesium could only diffuse into the quartz glass to produce a single MgO-rich layer and the nc-Si thin film (reaction (1)). Once the magnesium content exceeded the saturation point, the extra magnesium diffused into the nc-Si film and reacted with Si to produce Mg\(_2\)Si (reaction (2)).

\[
\begin{align*}
2\text{Mg} (\text{s}) + \text{SiO}_2 (\text{s}) & \rightarrow \text{Si} (\text{s}) + 2\text{MgO} (\text{s}) \quad \text{(1)} \\
2\text{Mg} (\text{s}) + \text{Si} (\text{s}) & \rightarrow \text{Mg}_2\text{Si} (\text{s}) \quad \text{(2)}
\end{align*}
\]

The MgO and Mg\(_2\)Si could be easily removed by the hydrochloric acid solution after the reaction process, and therefore the amount (thickness) of silicon decreased as the magnesium content was further increased. To estimate the average grain size (\(d\)) and the crystalline volume fraction (\(F\)) of the nc-Si thin film, equations (3)\(^ {21}\) and (4)\(^ {22}\) were used.

\[
d = 2 \pi \left( \frac{B}{\Delta \omega} \right)^{1/2} \quad \text{(3)}
\]

\[
F = \frac{I_a + I_b}{(I_a + I_b + I_c)} \quad \text{(4)}
\]

In equation (3), the term \(\Delta \omega\) represents the peak shift observed for the nc-Si when compared with single-

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Peak shift (cm(^{-1}))</th>
<th>Grain size (nm)</th>
<th>Crystalline volume fraction (at.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>516</td>
<td>4.7</td>
<td>85</td>
</tr>
<tr>
<td>T2</td>
<td>516</td>
<td>4.7</td>
<td>86</td>
</tr>
<tr>
<td>T3</td>
<td>515</td>
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<td>T4</td>
<td>515</td>
<td>4.2</td>
<td>93</td>
</tr>
<tr>
<td>T5</td>
<td>515</td>
<td>4.2</td>
<td>88</td>
</tr>
</tbody>
</table>
Investigation on a magnesiothermic reduction process.  

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The approach for the production of nc-Si thin films was tested in this work which is based on a magnesiothermic reduction reaction. The SEM and EDS results showed that the surface of a quartz glass substrate could be successfully converted into a silicon thin film. The Raman analysis and the band gap estimated from the UV–visible absorption spectra (2.94 eV) confirmed that nc-Si films were fabricated. Above all, the Raman analysis further revealed that the amount of silicon produced in the thin film form (i.e., the film thickness) and the crystalline volume fraction strongly depend on the initial magnesium content (i.e., the nominal thickness of the deposited magnesium film). The thickness of the silicon thin film and its crystalline volume fraction were observed to first increase with the magnesium content until reaching a maximum and then to decrease as the magnesium content was further increased. This is attributed to the production of Mg2Si once the magnesium content exceeds a certain saturation level. The grain size of the nc-Si thin film was found to be determined by the reaction time and did not depend on the magnesium content.

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References


