Magnesium silicide film on a silicon substrate prepared by electrochemical method in LiCl-KCl

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The method as described below enables us to synthesize a continuous film of Mg$_2$Si with the thickness up to 10 $\mu$m. By conducting potentiostatic electrolysis of a silicon cathode in a molten LiCl-KCl-MgCl$_2$ melt, electrochemical formation of magnesium silicide proceeded according to the following reaction steps:

$$\text{Mg(II)} + 2e^- \rightarrow \text{Mg} \quad \text{(Reduction of Mg(II) on a Si cathode)},$$

$$2\text{Mg} + \text{Si} \rightarrow \text{Mg}_2\text{Si} \quad \text{(Formation of silicide film)}.$$  

From XRD and SEM results, a polycrystalline Mg$_2$Si with a thickness of 20 $\mu$m was uniformly formed on Si (001) surface, after conducting potentiostatic electrolysis at 0.8 V (vs. Li$^+/\text{Li}$). Absorption edge of the sample was exhibited at around 0.8 eV through transformation of reflectance spectra with Kubelka-Munk function.

Key words: Energy conversion, Environmentally friendly materials, Non-conventional electrolysis, Molten salt, Solar cell

1. INTRODUCTION

Various functional materials have been developed to be applicable to energy and electric fields. Many researchers have thus successfully developed formation processes of functional materials. However, some processes are inapplicable for producing functional materials without harmful materials and high energy. From the background, a new formation process of functional materials using electrochemical methods in molten salts, which does not require harmful materials and high energy, has been proposed and developed by the authors group. In addition, the attractive aspects of the method is that it is possible to form functional materials, which is considered to be difficult to form conventional methods such as chemical vapor deposition, physical vapor deposition, and so on. In this paper, we illustrate the principle of the electrochemical formation of functional film with Mg$_2$Si film formation. Binary silicide semiconductor films (e.g., Mg, Ca, Fe, Mn - Si) have been attracted intensive studies for the last few decades, since they are anticipated to reveal excellent optical properties in contract to those of crystalline or amorphous silicon films [1]. In addition, silicides involving environmentally friendly elements are an advantage from the ecological point of view. To realize these excellent properties of silicide, many formation processes have been developed such as reactive deposition epitaxy (RDE) [2], thermal vapour deposition process [3], chemical silicidation process [4] and silicide powder-sintering process [5]. Though some of them have been already available on industrial scales, it is still difficult to achieve the growth of their continuous film layer of a few micrometers thick with large area of complicated surface. Thus, a new simple process is necessary for producing silicide films with the thickness of the order of $\mu$m and controlling the compositions.

Here, we propose a novel electrochemical formation process using cathodic reduction of metal cations according to the following manner. Molten chloride melts (450-750 K) containing metal chloride (MCl$_x$) are used as electrolytes and MCl$_x$ is decomposed in chloride melts into $\text{M}^{x+}$ and Cl$^-$. A silicon electrode (Si) is used as a cathode electrode and is cathodically polarized to promote electrochemical reduction according to the following reaction steps:

$$\text{M}^{x+} + xe^- \rightarrow \text{M} \quad \text{(Reduction of M}^{x+} \text{on Si cathode)}, \quad (1)$$

$$x\text{M} + \text{Si} \rightarrow \text{M}_x\text{Si} \quad \text{(Formation of silicide film).} \quad (2)$$

The key feature of this process is that the continuous film formation and growth rate of the obtained silicides are controlled by the electrolytic conditions (applied potentials, current densities). In addition, the simple apparatus without harmful chemicals is available.

In order to confirm the feasibility of the above electrochemical process as a new process for producing silicide films, a magnesium silicide was selected for investigation. First, the electrochemical behaviour of magnesium ions in a LiCl-KCl melt was investigated by means of electrochemical measurements. Based on the electrochemical data, the electrochemical formation of magnesium silicide in molten LiCl-KCl was carried out on a silicon wafer. After the electrolysis, the products were analyzed by means of X-ray diffraction, surface SEM image and cross-sectional SEM and XPS. Optical properties of the obtained samples were also measured by a visible-ultra violet spectroscopy. Through the experimental results, we clarified the relationships between magnesium silicide and electrolytic conditions.

2. EXPERIMENTAL

All experiments were conducted in an argon atmosphere using a glove box with a continuous gas-refining instrument (Japan Piones Co., Ltd.: MBN-R-07). The experimental setup used was the same.
as previously reported \(^6\). The solvent was a binary eutectic mixture of LiCl-KCl prepared from vacuum dried reagent grade chemicals (Wako Pure Chemical Co., Ltd.). Magnesium dichloride (MgCl\(_2\)) (Wako Pure Chemical Co., Ltd.) was added directly into the melt as bivalent magnesium cation (Mg(II)) source. Si (99.99 %) was used as the working electrode. A glassy carbon rod was used as the counter electrode. The reference electrode was a Li-Al alloy in the coexisting (\(\alpha+\beta\)) phase state prepared electrochemically from an aluminum wire (20 mm \(\phi\) 1 mm, The Nilaco Co., Ltd. 99.99 %). The potential of this electrode shows the equilibrium potential of the following reversible reaction: \(^7\)

\[
\text{Al}(\alpha) + \text{Li}^+ + e^- = 2\text{Li}_{0.5}\text{Al}_{0.5}(\beta)
\]  

(3)

A dynamic reference electrode using electrochemically deposited lithium was used to correct the potential measured by the Li-Al alloy reference electrode. All potentials in this paper are referred to this potential and shown as [V vs. Li\(^+/\text{Li}\)] \(^8\). Electrochemical measurements were conducted using a potentiostat/galvanostat combined with a function generator (Hokuto Denko Co., Ltd.: HZ-3000). The obtained films were characterized by X-ray diffraction (XRD) (Rigaku Co., Ltd.: Multiflex) using Cu K\(\alpha\) line as the X-ray source. Measurements of surface chemical states and depth profiles were performed by an X-ray photoelectron spectroscopy (XPS) (Shimadzu Co., Ltd.: ESCA-3200-01) using Mg K\(\alpha\) line as the X-ray source. Morphologies of samples were observed through a scanning electron microscope (SEM) (Hitachi Co., Ltd.: S-2300). The measurement of the nitrogen concentration profiles was also conducted by an electron probe microanalyser (EPMA) (Horiba Co., Ltd.: EMAX-2200). Optical absorption coefficient spectra at room temperature were obtained through transformation of reflectance spectra with Kubelka-Munk function \(^9\).

3. RESULTS AND DISCUSSION

3.1 Electrochemical behaviour of magnesium ions

Cyclic voltammetry was carried out at a silicon electrode in LiCl-KCl-MgCl\(_2\) (0.1 mol\%) in order to study the electrochemical behaviour of magnesium related to the electrochemical formation of silicide. Figure 1 shows a cyclic voltammogram of silicon in LiCl-KCl containing 0.1 mol\% MgCl\(_2\) at 723 K. The sharp increase of cathodic currents at about 0.7 V and the corresponding anodic currents at about 0.8 V are observed, which are attributable to the formation of magnesium metal and its dissolution. The potential agrees with the reported value of Mg(II)/Mg \(^10\). On the cathodic scan, cathodic currents are also observed at potential region from 1.2 to 0.8 V. Since this value is more positive than the potential of magnesium metal deposition, the cathodic currents are considered to associate with the formation of Si-Mg alloy. Taking the binary phase diagram of a Si-Mg system \(^11\) into account, Mg\(_2\)Si is an only intermetallic compound in the Mg-Si system. Thus, the cathodic currents at 1.2 V - 0.8 V are considered to correspond to the Mg\(_2\)Si formation as shown in overall reaction (4):

\[
\text{Si} + 2\text{Mg(II)} + 4e^- = \text{Mg}_2\text{Si}
\]  

(4)

Further electrochemical measurement was carried out by means of chronopotentiometry. A chronopotentiogram of Figure 2 shows two plateaus at about 0.85 V and 0.65 V, which corresponds to reaction (4) and an electrochemical reaction of Mg(II)/Mg couple, respectively. From the voltammetric and chronopotentiometric results of Figures 1 and 2, potentiostatic electrolysis was conducted at 0.8 V, which potential is negative enough to form magnesium silicide on a silicon substrate.

3.2 Electrochemical formation of magnesium silicide

Based on the voltammetric data, a single crystal of silicon was used as the cathode and potentiostatic electrolysis of the cathode was carried out at 0.8 V for 3.0 h in LiCl-KCl containing 0.1 mol\% MgCl\(_2\) at 723 K. After conducting potentiostatic electrolysis, the surface color of the sample turned light gray, which suggests the formation of magnesium silicide.

Chemical analysis of surface was carried out by XPS, combined with argon ion sputtering for depth analysis. The binding energies at peak positions of Mg 2s spectra and Si 2p spectra were observed. These results showed that the sample surface composed of magnesium atoms and silicon atoms. Figure 3 shows XRD pattern of a silicon electrode surface after potentiostatic electrolysis at 0.8 V for 3.0 h. The main diffraction peaks in Fig. 3 coincide with those from a face-centered cubic structure of CaF\(_2\). The obtained film
is a polycrystalline Mg$_2$Si film from the diffraction pattern. Figure 4 (a) and (b) shows a top view and a cross-sectional view, respectively, of the sample after potentiostatic electrolysis at 0.8 V for 3 h. From Fig 3 (a), the sample is completely covered with homogenous Mg$_2$Si film. It is found from Fig. 4 (b) that the film has no crack through the obtained film and Mg$_2$Si film is continuously grown on a silicon substrate with thickness of about 20 $\mu$m. This indicates that a growth rate of Mg$_2$Si film on a silicon substrate is about 6 $\mu$m h$^{-1}$.

Fig. 3 XRD pattern of a sample after potentiostatic electrolysis at 0.8 V for 3 h in LiCl-KCl containing 0.1 mol% MgCl$_2$ at 723 K.

(a)

(b)

Fig. 4 (a) A surface and (b) a cross-sectional SEM image of a silicon substrate after conducting potentiostatic electrolysis at 0.8 V for 3 h in LiCl-KCl containing 0.1 mol% MgCl$_2$ at 723 K.

3.3 Optical properties

The reflectance was measured by a spectrometer. The Kubelka-Munk function\[^9\]:

$$\alpha/s = (1-R_d)^2 / 2R_d$$  \hspace{1cm} (5)

was used to convert the diffusion reflectance, $R_d$, into an optical absorption coefficient, $\alpha$. The scattering coefficient, $s$, is less dependent of energy at least near the bandgap where the absorption intensity is low and the peak position never change. As shown in Fig. 5, a large absorption was observed at 0.8-1.2 eV, which is absent in Si. Absorption edge was exhibited at around 0.8 eV. Assignments of optical transitions were given to the absorption bands by using conventional reports. The absorption bands at 1.9 and 2.6 eV are consistent with direct transitions in reported reflectance measurements for single crystals\[^12\] and results of band calculations\[^13\]. The absorption at the band edge, which is claimed to be indirect transition from the calculations, contains substantial direct absorption. It is suggested that the direct absorption begins at 0.77 eV just below the indirect absorption edge, which is located at 0.83 eV.

Fig. 5 The optical absorption coefficient of Mg$_2$Si derived from Kubelka-Munk equation.

4. CONCLUSION

In order to illustrate the principle and feasibility of the above electrochemical process as a new process for producing functional materials, magnesium silicide was selected as a model case. Electrochemical formation of magnesium silicide has experimentally been confirmed by using the cathodic reduction of magnesium ions in molten LiCl-KCl-MgCl$_2$ (0.1 mol%) melt at 723 K according to the following reaction:

$$\text{Si} + \text{Mg(II)} + 4e^- = \text{Mg}_2\text{Si}. \hspace{1cm} (6)$$

From the XRD analysis, a polycrystalline Mg$_2$Si was formed on Si (001) surface, after conducting potentiostatic electrolysis at 0.8 V (vs. Li$^+$/Li). It was found from SEM images that the obtained continuous film layer had uniformly a thickness of about 20 $\mu$m. Optical absorption coefficient spectra at room temperature were obtained through transformation of reflectance spectra with Kubelka-Munk function. A large absorption was observed at 0.8-1.2 eV, which is absent in Si. Absorption edge was exhibited at around 0.8 eV. We confirmed that the novel electrochemical process of silicide semiconductor films on a silicon substrate, which enable us to synthesize a continuous silicide film layer with thickness of the order of micrometers other than magnesium silicide.
5. REFERENCES


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