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Crystallization of Amorphous Silicon Thin Films Using a Viscous Nickel Solution

Jin Hyung Ahn and Byung Tae Ahn*,z

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Yusung-gu, Taejon 305-701, Korea

A viscous Ni solution was applied on amorphous Si films and its effect on the crystallization of amorphous Si films was investigated. A viscous Ni solution was prepared by dissolving $NiCl_2$ in 1 N HCl and mixing it with propylene glycol. $NiCl_2$ and Ni was uniformly deposited by spin coating and drying the viscous metal solution, and it enhanced the crystallization at lower temperature overcoming the nonuniform coating of diluted acid metal solution. The a-Si films deposited by low pressure chemical vapor deposition with Si_2H_6 were fully crystallized in 10 h at 500°C by furnace annealing and in 8 h at 480°C by microwave annealing. The enhanced crystallization was due to the mediation by $NiSi_2$. The surface roughness of the crystallized Si films using the Ni solution was smoother than that of the crystallized Si films with Ni metal layer.
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Polycrystalline Si (poly-Si) thin films have many applications in making electronic devices like thin film transistors (TFTs), solar cells, and image sensors. Poly-Si thin films are generally fabricated by crystallizing amorphous Si (a-Si) thin films because it can render larger grains than those of directly deposited poly-Si films.[1] Excimer laser annealing and solid phase crystallization (SPC) are widely used to crystallize a-Si films. The SPC, in which a-Si films are annealed without melting, is simple and more uniform. But, the SPC process generally takes tens of hours to crystallize a-Si films at 600°C, which is too high temperature for large area glass substrates. The SPC crystallization temperature has been lowered by annealing a-Si films in contact with metals on the surface, called metal-induced crystallization or silicide-mediated crystallization. Interfacial reactions between Si and metals (Au, Cu, Al, Ni, Pd) have occurred at low temperature.[2-6] Hayzelden *et al.* studied the nucleation and growth mechanism of $NiSi_2$-mediated enhanced crystallization using Ni-implanted a-Si films through *in situ* transmission electron microscopy (TEM) observation.[7] Lee *et al.* fabricated high performance thin film transistors by laterally crystallizing the channel area from the source/drain on which 5 Å thick Ni film was deposited by sputtering.[8]

Metals like Ni can be deposited by sputtering, evaporation, or ion implantation. But metals also can be applied from metal solutions. Metal solutions were utilized to enhance the crystallization of a-Si films.[9-11] They all used a diluted acid such as HCl and HNO_3 as the solvent. The coating of a metal solution on Si films is simple and metal solutions can well control the amount of metals deposited on a-Si films through the metal concentration in the solution. But the diluted acid solutions have some problems. Metals such as Ni and Al of which electronegativity is not larger than Si cannot be effectively deposited on the Si surface.[12] Furthermore, the solution on a-Si films exists in uncontrollable forms of droplets because the Si surface is hydrophobic, resulting in nonuniform and irreproducible deposition.

In this study, a viscous Ni solution dissolving $NiCl_2$ in 1 N HCl + propylene glycol (PG) was prepared to overcome these problems. PG is a viscous organic solvent that has been used in producing slurries for a screen printing process.[13] The deposition behavior of $NiCl_2$ and Ni from the viscous Ni solution and the crystallization behavior of a-Si film with the solution coating were investigated. The viscous solution enabled the uniform crystallization of a-Si films at lower temperatures.

Experimental

100 nm thick a-Si films were deposited by low pressure chemical vapor deposition (LPCVD) at 530°C using Si_2H_6 on oxidized Si wafers. The films were cleaned in boiling H_2SO_4 + H_2O_2 solution, dipped in a diluted HF solution to remove oxide on the surface, and coated with a viscous solution. The viscous Ni solution was prepared by dissolving $NiCl_2$ in 1 N HCl and mixing with PG. The volumetric ratio of 1 N HCl and PG was fixed to 1:4. The solution was spin coated and dried in oven at 230°C in N_2. Then, the a-Si films were crystallized in Ar in a tube furnace or in a microwave heating system. Intrinsic a-Si and a-Si films with Ni metal layer were also crystallized for the comparison.

The microwave heating system consisted of a microwave generator, a heating chamber, and temperature control systems. Microwaves were transferred to the chamber through a waveguide. The temperature was controlled by adjusting the microwave power continuously. The microwave frequency was 2.45 GHz. The thermocouple was in direct contact with the back side of the Si wafer.[14]

Surface morphologies of Si films were observed by optical microscope and scanning electron microscope (SEM). The chemistry of the deposited materials on Si films after oven dry and after crystallization were investigated using X-ray photoelectron spectroscopy (XPS) with Al Kα X-ray source (1486.6 eV). The top surface of the oven-dried sample and crystallized sample were sputtered off for 1 min before the XPS analysis to determine the bulk composition of thin film. And binding energy was determined by referencing to the C 1s line at 284.8 eV. Secondary ion mass spectroscopy (SIMS) was used to investigate the distribution of Ni and Cl in the crystallized Si films. The crystalline fraction of the annealed Si films was evaluated with Si(111) peak intensity of X-ray diffraction. The amount of Ni species applied on Si films was measured by soaking the $NiCl_2$ coated Si sample in 1% HNO_3 solution and then analyzing the amount of Ni in the solution with inductively coupled plasma mass spectroscopy (ICP-MS). Microstructures and surface roughness of the poly-Si films were measured with TEM and atomic force microscopy (AFM), respectively.

Results and Discussion

Figure 1 shows the optical microscopic surfaces of LPCVD Si films after crystallization at 500°C for 10 h after spin coating the 1,000 ppm (0.017 M) Ni 1 N HCl solution (Fig. 1a) and spin coating and drying 0.1 M Ni 1 N HCl + PG viscous solution (Fig. 1b) on the a-Si film. Lumps of adsorbate are seen in Fig. 1a (arrows). The diluted acid solution exists in an uncontrollable form of droplets because the Si surface is hydrophobic. The lumps originated from the agglomeration of the solute as the droplets of Ni solution dried. Only the a-Si film around the lumps is crystallized, while the other region remain amorphous. Ni is not expected to be deposited on Si because the electronegativity of Ni is not larger than that of Si.[12] So,

* Electrochemical Society Active Member.
z E-mail: btahn@kaist.ac.kr

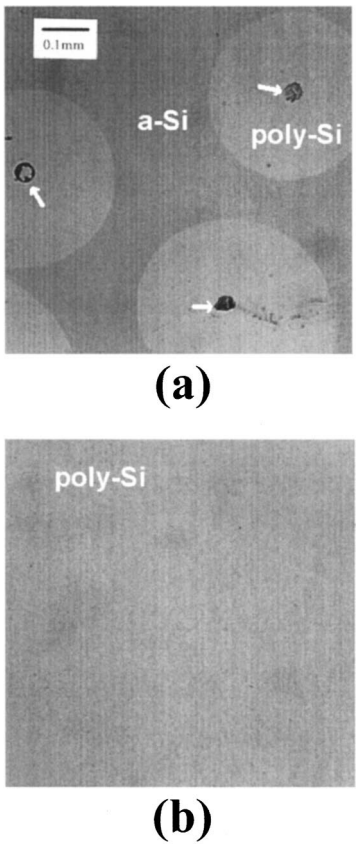

Figure 1. SEM surface micrographs of Si films after annealing at 500°C for 10 h. (a) Ni was adsorbed from 1,000 ppm Ni 1 N HCl solution; (b) Ni was adsorbed from 0.1 M Ni (1 N HCl + PG) solution.

the coating of a diluted acid solution results in a nonuniform and irreproducible deposition of Ni species, causing a nonuniform crystallization.

By employing the viscous Ni solution, a uniform film instead of droplets was coated. No lumps of adsorbate were detected after drying the film even in SEM investigation. And enough amount of Ni is uniformly supplied from the coated layer so that Ni silicide-enhanced crystallization can be uniformly achieved as shown in Fig. 1b.

Figure 2 shows the XPS spectra of the Si films after oven-drying the viscous Ni solution and after crystallization at 530°C for 5 h in Ar. In the oven-dried film, Ni, Cl, and O exist as shown in Fig. 2a. The Ni 2p3/2 peak is located at 856.1 eV corresponding to $NiCl_2$ and 852.7 eV corresponding to Ni (Fig. 2b). The peak near 862 eV is a satellite peak. Also some of the Ni is associated with a NiO_x peak at the binding energy of 531.3 eV (Fig. 2c). The binding energies of Ni_2O_3 and NiO in the O 1s spectra have very similar value of 531.3 and 532.2 eV, respectively. Therefore, it can be said that $NiCl_2$, Ni, and NiO_x are deposited on the a-Si film after oven drying the viscous solution. After crystallization at 530°C, the Cl peaks completely disappeared and the intensities of oxygen peaks greatly increased (Fig. 2a). The absence of a Cl peak means the absence of $NiCl_2$. After crystallization, Ni 2p3/2 peak (Fig. 2b) shifted and broadened to lower energies of 855.8 and 854.4 eV, which correspond to Ni_2O_3 and NiO, respectively. This can be corroborated in the O 1s spectra (Fig. 2c). The NiO_x peak at 531.3 eV increased after annealing. The stronger intensity of the O 1s peak at 532.7 eV may arise from SiO_2. So, it can be said that $NiCl_2$ and Ni deposited on the a-Si surface reacts with oxygen and forms NiO_x during crystallization annealing. Note that Ni silicide is not detected in the XPS analysis even though $NiSi_2$ precipitates are detected in the Si films through TEM observation as shown later.

These oxides and other adsorbates such as carbon can be removed by a simple cleaning process: dipping in boiling H_2SO_4 + H_2O_2 solution and in diluted HF solution. The elements of these adsorbates, especially Ni, are below the detection limit of Auger electron spectroscopy (AES) after cleaning in the solutions. The removal of NiO_x is most likely by the lift-off process of the underneath SiO_2 layer. Figure 3 shows the SIMS depth profiles of Ni and Cl in the poly-Si film after crystallization at 530°C for 5 h and removal of the surface oxide adsorbates. Ni is incorporated into the bulk of the film and is accumulated at the Si/SiO_2 interface. When a-Si film with Ni metal layer was annealed, the same result was reported.[15] Cl is also incorporated into Si film and is uniformly distributed. From the XPS and SIMS results, it can be said that most of the $NiCl_2$ and Ni deposited on Si was converted to NiO_x during the annealing and only a small amount of Ni is incorporated into Si and enhances the low temperature crystallization.

Figure 4 shows the crystalline fraction as a function of annealing time at various annealing conditions. Since the a-Si film was deposited from Si_2H_6 gas, it generally took about 30 h to fully crystallize at 600°C in a tube furnace. The a-Si films on which the 0.1 M viscous Ni solution was spin coated and dried are fully crystallized in 10 h at 500°C in a tube furnace, even though the annealing temperature is 100°C lower. And the a-Si films using the viscous Ni solution are fully crystallized in about 8 h at 480°C by microwave annealing. Lee reported that the crystallization of plasma enhanced PECVD a-Si was enhanced by microwave annealing.[14] The employment of viscous Ni solution enabled us to lower crystallization temperature from 600 to 480°C. Furthermore, a uniform and reproducible film can be produced by employing the viscous solution. The enhanced crystallization of a-Si by employing the viscous Ni solution clearly overcame the limitation of employing the diluted acid metal solution.

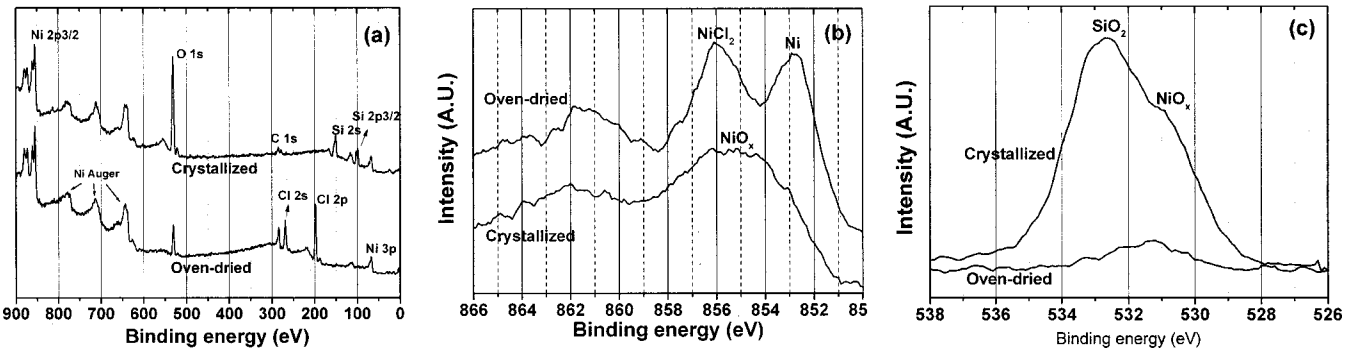

Figure 2. XPS spectra of the surface of the as-coated Si film and the annealed (530°C, 5 h) Si film. (a) The results of wide-scan, (b) Ni 2p3/2 peak, and (c) O 1s peak.

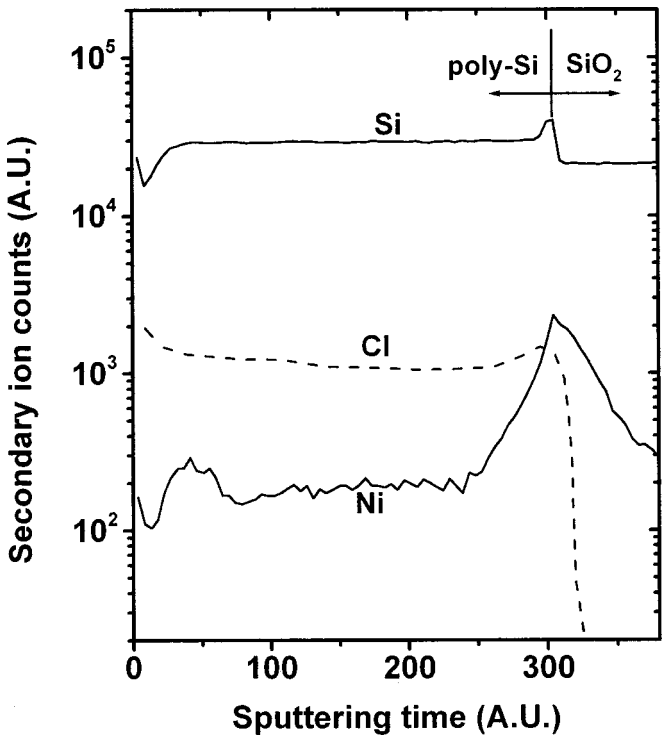

Figure 3. SIMS depth profile of Ni and Cl in the poly-Si films.

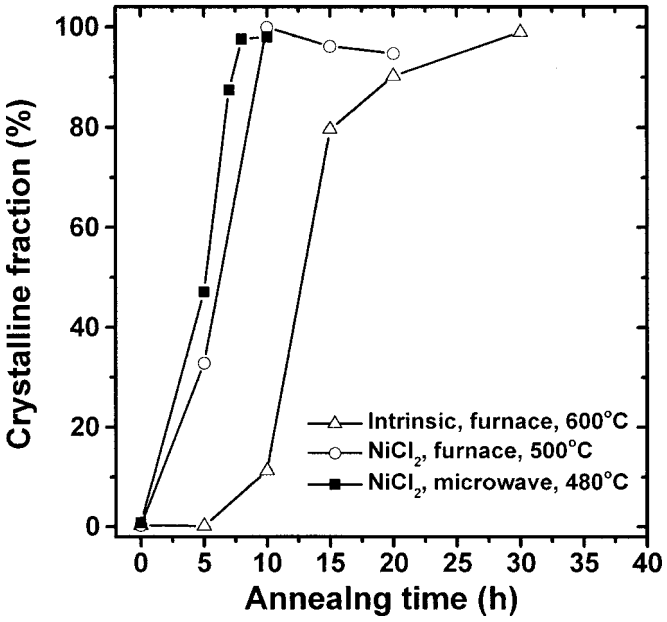

Figure 4. Crystalline fraction as a function of annealing time: a-Si films without Ni adsorption (annealed at 600°C), a-Si films with Ni deposition from 0.1 M Ni (1 N HCl + PG) solution (annealed at 500°C) annealed in a furnace and a-Si films with Ni deposition from 0.005 M Ni (1 N HCl + PG) solution (annealed at 480°C) annealed in a microwave annealing system.

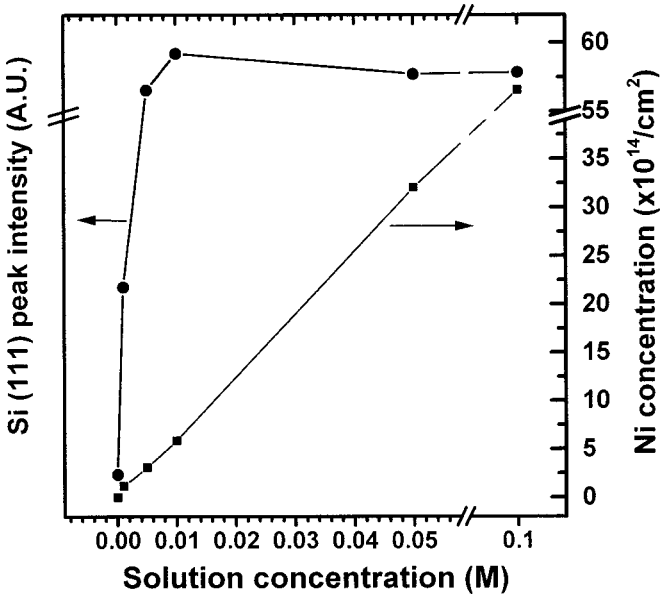

Figure 5. Concentration of Ni adsorbed on Si films and Si crystalline fraction of Si films annealed at 500°C for 10 h as a function of the concentration of Ni 1 N HCl + PG solution.

Figure 5 shows the Ni concentration on as-deposited a-Si films as a function of the Ni concentration in the viscous solution. The Ni concentration on the surface increased from 1.2×10^{14} to 5.7×10^{15} cm^{-2} as the Ni solution concentration increased from 0.001 to 0.1 M. The Ni concentration on the surface was linearly proportional to the Ni solution concentration, but the concentration on the surface from the 0.001 M solution was about two times higher than expected. This is probably due to the experimental errors caused by weak intensity of ICP-MS when the sample is too weak. For diluted acid metal solutions, metal ions are deposited on Si surface by accepting electrons from Si atoms. In the process, the reaction in which Si releases electrons depends on pH of the solution as well as the concentration of the solution.[12] But for the viscous Ni solution, the amount of deposition is dominated by a physical process that the deposited Ni concentration is linearly proportional to the metal solution concentration. Therefore, the amount of metal deposited on a-Si film can be well controlled by solution concentration for the application purpose.

Figure 5 also shows the crystalline fraction of Si films annealed at 500°C for 10 h in a tube furnace as a function of Ni solution concentration. The a-Si films are fully crystallized when the solution concentration is above 0.01 M, where the corresponding Ni concentration before annealing is 5×10^{14} cm^{-2}. It is desirable to employ as small a Ni solution concentration as possible to avoid metal contamination in TFT applications.[12]

To understand how the crystallization was enhanced, the microstructure changes during crystallization have been investigated using TEM. Figure 6 shows the TEM images of partially and fully crystallized Si films using the viscous Ni solution. At the initial stage of crystallization, needle-like grains are formed and the widths of grains are about 0.15 μm. It is known that dendritic or elliptical grains form in intrinsic a-Si films.[16-18] Therefore, the nucleation and growth mechanisms of Ni-species-applied a-Si film and intrinsic a-Si films are different. The crystallization mechanism of intrinsic a-Si films was reported by several researchers.[17-19] Kim reported that crystalline nuclei had circular shapes originally, but the shape changed to an ellipse that contained twins at the center along the long axis. The twins assisted grain growth along the twin directions. Hayzelden *et al.* studied the mechanism of MIC using Ni through TEM including *in situ* observation.[7,20,21] They reported that Ni reacts with Si to form $NiSi_2$ precipitates and crystalline Si nucleates at the surface of $NiSi_2$ precipitates. And the crystalline nuclei grow by the supply of Si from a-Si through $NiSi_2$ precipitates which migrate through the a-Si film, resulting in needle-like grains. In the crystallization of a-Si using the viscous Ni solution, the growth mechanism seems the same as that of Ni-metal coated a-Si. No dendritic or

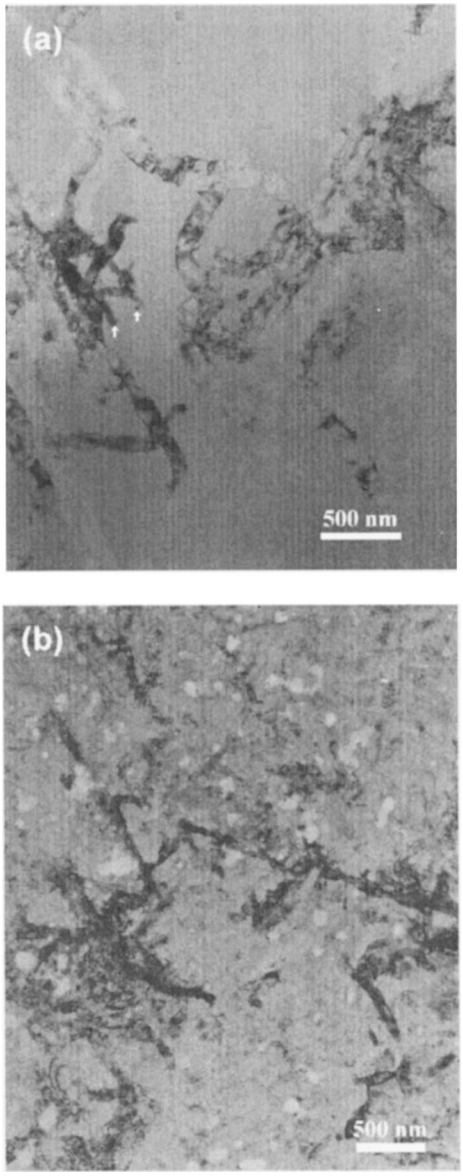

Figure 6. Microstructures of (a) partially crystallized Si film and (b) fully crystallized poly-Si film with NCl_2 coating.

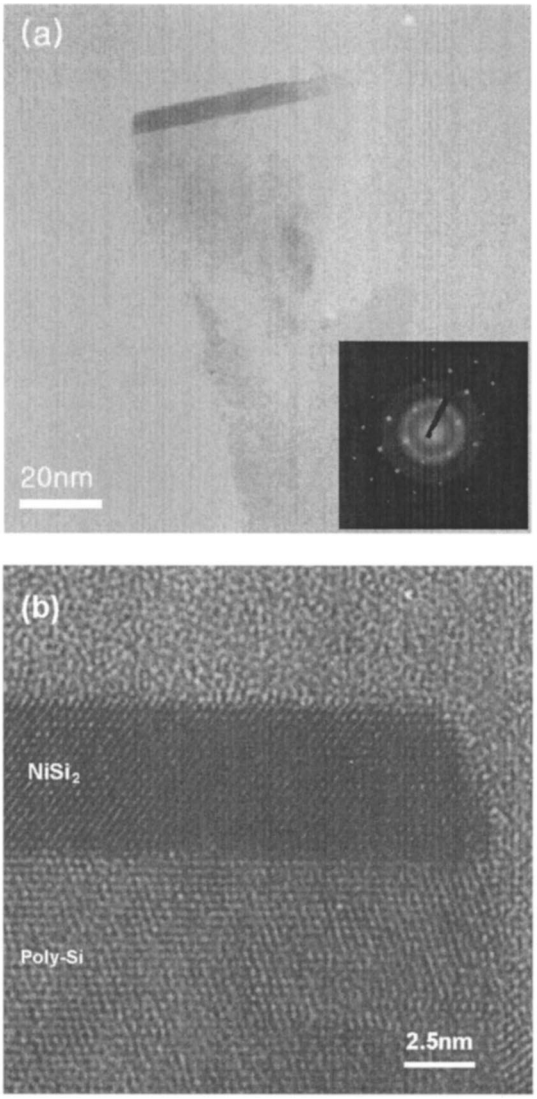

Figure 7. Ni silicide precipitate at the edge of a Si grain (a), and its high resolution TEM image (b).

elliptical grain is found in the fully crystallized film as well as in the partially crystallized film.

Figure 7 shows the edge of needle-like grains like those designated with arrows in Fig. 6a and its high resolution image. A darker plate with the thickness of about 6 nm was detected. Ni was detected in energy dispersive X-ray spectroscopy analysis of the dark plate (15.1 atom %), indicating that a Ni silicide exists at the a-Si and c-Si interface. And the lattice and diffraction patterns of the dark plate and crystalline Si coincide well in the image (Fig. 7). The dark Ni silicide phase and the crystalline Si have an epitaxial relation with small lattice mismatch. The HRTEM lattice image and diffraction pattern indicate that the dark plate is $NiSi_2$ which is almost isomorphic and has very small lattice mismatch with crystalline Si. Our TEM observation indicates that the crystallization of a-Si using the viscous Ni solution is also a Ni-silicide mediated process, like that of a-Si films with Ni metal film deposition. Ni, which comprises $NiSi_2$ precipitates, would have come from $NiCl_2$, not only from Ni, as $NiCl_2$ was decomposed during the annealing.

The a-Si film with 5 Å Ni metal film deposition was fully crystallized even in 3 h at 500°C, while it took about 10 h for the a-Si film using the 0.005 M viscous Ni solution. The crystallization of a-Si films using the viscous Ni solution was slower than that of a-Si films with Ni metal film deposition. But the surface of the poly-Si film using the viscous Ni solution was not roughened after crystallization, while that with Ni metal film deposition was significantly roughened. Figure 8 shows the AFM surface images of the poly-Si films crystallized from (a) a-Si using the 0.1 M viscous Ni solution and (b) a-Si with Ni metal film deposition (2 nm thick). The amount of Ni on Si surface was similar. The surface roughness of the LPCVD a-Si film was 19 Å in root mean square (rms) value. The surface roughness of poly-Si films using the viscous Ni solution and Ni metal film deposition were 18 and 61 Å in rms value, respectively. The reason for this phenomenon is now uncertain, and needs to be studied. However, the flat Si surface is desirable for higher mobility TFT devices.

Conclusions

A uniform coating of $NiCl_2$ and Ni on a-Si film was possible by employing a viscous Ni metal solution instead of a diluted aqueous Ni solution. The viscous Ni solution was prepared by dissolving $NiCl_2$ in the mixture of 1 N HCl and propylene glycol. $NiCl_2$ and Ni were deposited on a-Si film after oven drying. The $NiCl_2$ and Ni mostly converted to NiO_x during annealing at 500°C. Some of Ni

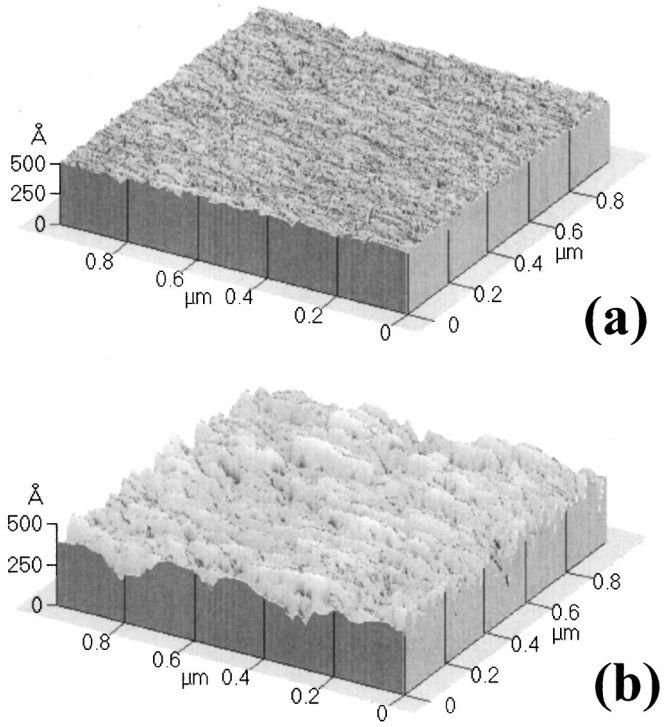

Figure 8. AFM images of (a) the surface of the poly-Si film with Ni deposited from 0.1 M Ni (1 N HCl + PG) solution and (b) that of the poly-Si film with 20 Å thick Ni metal film.

and Cl were incorporated into Si films, and Ni was accumulated at the Si/SiO_2 interface. Employing the viscous Ni metal solution enhanced the low temperature crystallization and enabled a uniform crystallization to occur. The amount of Ni applied on a-Si films was linearly proportional to the Ni solution concentration. But the crystallization was saturated at some concentration of the solution. The crystallization enhancement was mediated by $NiSi_2$, like a-Si film with a Ni metal layer. The surface roughness of the crystallized Si film using the viscous Ni solution was smoother than that of the crystallized Si films with Ni metal film deposition, providing better interface quality between Si/SiO_2 for TFT applications.

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