Crystallization of Amorphous Silicon Thin Films Using Self-Limiting ALD of Nickel Oxide

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The crystallization of amorphous Si (a-Si) thin films was performed using atomic layer deposition (ALD) of nickel oxide. Nickel oxide layers were deposited using nickel aminoalkoxide as a precursor in Ni and water as a precursor in oxygen. The presence of nickel oxide caused significant crystallization to occur in a-Si at 575°C under a reducing atmosphere. Even one single ALD layer of nickel oxide was found to be high enough to crystallize the a-Si thin films. Self-limiting layer controllability in ALD is useful in providing a catalytic layer for formation of polycrystalline Si thin films for application to large-scale flat panel displays.

Low-temperature polycrystalline Si (LTPS) technology has opened up innovative approaches for fabricating next-generation displays due to the higher mobility of charge carriers, 10–100 cm²/V s, compared to that of the conventional a-Si-based transistors, only 1 cm²/V s. The polycrystalline Si-based transistors allow a wide range of applications including liquid crystal displays, organic light-emitting diodes (OLEDs), systems-on-glass (SOG), etc., in terms of switching and even driving circuits. The combination of OLEDs or SOG requires a stringent control of the transistor parameters such as threshold voltages, mobilities of the charge carriers, S, slopes, and leakage currents. The success of LTPS transistors relies to a large extent on the polycrystalline Si channel thickness of nickel oxide is extremely significant in determining the device characteristics of the LTPS transistors. Various approaches have been reported with the aim of achieving a large grain size, including solid phase crystallization (SPC), metal-induced crystallization (MIC), excimer laser annealing (ELA), and field-aided crystallization using a high electrical field. Excimer laser annealing has initiated the commercialization of LTPS transistors in spite of a high manufacturing cost and operational difficulties in controlling the optical components. Although metal-induced crystallization has been suggested as a technique for lowering the manufacturing cost and obtaining an adequate transistor yield, MIC using Ni suffers from high leakage current due to the inability to control the metal agents, typically a high level of Ni contaminants. In order to reduce the Ni content, metal-induced lateral growth has been introduced. Atomic layer deposition (ALD), as a deposition process by self-limiting mechanism, has opened up new opportunities in thin-film deposition due to a superior control of thickness and uniformity, a low thermal budget, excellent step coverage, etc. The only drawback that has been mentioned is sluggish deposition rates of usually less than 2–3 Å/cycle, due to the inherent alternating deposition of two different reactive species. No previous work to date on ALD has been reported on the crystallization of a-Si thin films in conjunction with LTPS technology.

In this work, the self-limiting mechanism of ALD was attempted in the crystallization of a-Si thin films on glass substrates, in combination with the atomic control of Ni atoms into the underlying thin films. To gain insights into the role of ALD of nickel oxide, the crystallization of a-Si thin films was monitored using UV-visible (UV-vis) spectrophotometry, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The implications of ALD of Ni species in the crystallization of a-Si thin films are discussed in conjunction with active matrix OLEDs.

Amorphous silicon thin films of 500 Å were deposited on glass substrates coated as a thin SiO₂ buffer layer (of 3000 Å thickness) using plasma-enhanced chemical vapor deposition; the SiO₂ layer functions as the diffusion barrier against detrimental mobile ions originating from glass substrates. The deposited specimens are cut into square-shaped plates (10 mm × 10 mm or 20 mm × 20 mm). A commercial ALD reactor (Genitech, Inc., Daejeon, Korea) was employed to deposit the nickel oxide films. The current ALD employed Ni(dmamb)₂ as a precursor in Ni, where dmamb is described as 1-dimethylamino-2-methyl-2-butanolate, (–OCMeEtCH₂NMe₂) and water as a precursor in oxygen. One basic ALD cycle was performed according to the standard sequence: A[Ni(dmamb)₂; supply: 4 s]–[Ar purge: 5 s]–B[H₂O supply: 3 s]–[Ar purge: 5 s]. The self-limiting process was repeated to the predetermined number of cycles: 1, 2, 5, and 10. The substrate temperature was kept at 140°C. Through thickness monitoring on nickel oxide films prepared through 100 ALD cycles, the growth rate was estimated to be approximately 1.4 Å per cycle. The film thickness of nickel oxide is expected to range from about 1.4 to 14 Å, depending on the ALD cycle.

During the annealing steps, a forming gas (H₂/N₂ mixture) was employed in order to promote crystallization in a-Si thin films. The annealing steps incorporated reference materials using the a-Si thin films not subjected to the ALD of nickel oxide in order to confirm the crystallization solely due to nickel-induced crystallization. Raman spectroscopy (LabRam HR, Jobin Yvon, Villeneuve d’Asq, France) and UV-vis spectrophotometry (UV-2450, Shimadzu, Kyoto, Japan) were applied in order to monitor the crystallinity before and after annealing the samples at 575°C for 1 h in Si. XPS (ESCALAB MK II, VG Scientific, Ltd., East Grinstead, England) was employed to confirm the chemical state of nickel oxide on the Si thin films and estimate trace amounts of Ni in Si. The detailed microstructure was investigated using high-resolution TEM (JEM-2000EX, JEOL, Tokyo, Japan).

A noticeable difference in crystallization was apparent with and without nickel oxide deposited through a series of Ni(dmamb)₂–H₂O ALD cycles in ALD, as shown in Fig. 1 and 2.
The optical transmission of crystallized Si thin films was enhanced quite significantly compared to that of a-Si thin films, independent of the ALD cycle numbers, i.e., film thickness. The crystallinity in a-Si thin films was confirmed through electron microscopy: a bright-field TEM image and electron diffraction in a-Si thin films (Fig. 2a) exhibit the amorphous state without nickel oxide, evidenced by lack of a distinct contrast in the bright field image and the absence of electron diffraction spots even after thermal treatments at 575°C. The opposite trend was found in nickel-induced crystallization, however, as shown in the dark field image of Fig. 2b. A majority of the crystallized grains was distributed with a zone axis of [110], as evidenced through the corresponding electron diffraction pattern. The microstructure in crystallized Si thin films is a mixture of small and large grains on the micrometer scale. From the dark-field image of Fig. 2b, the large grain size is estimated to be approximately 1.01 μm. However, the smaller grains are also found, even though it is difficult to identify the respective sizes. Considering the distribution of the crystallized grains, the average grain size is expected to be smaller than the above value. In Fig. 2b, several regions are found as highly bright, which are recognized to be empty voids among crystallized Si thin films. Nickel silicides can be dissolved in hydrofluoric acid, upon preparing TEM specimens from the glass substrates. The void regions are believed to be nickel precipitates distributed in crystallized Si thin films. The precipitate size and the average distance are inherently dependent on the Ni concentration. The lower the Ni concentration, the lower the number of nickel silicide precipitates and the smaller the precipitate size. The level of Ni-based precipitates should be minimized in order to minimize the poor device characteristics and significant degradation, guaranteeing high mobility and low leakage currents in thin-film transistor characteristics.

Figure 3 shows XPS survey spectra before and after thermal treatment (575°C and 1 h) for one Ni(dmamb)_2-H_2O ALD cycle performed on the a-Si thin films at 140°C, denoted by A and B, respectively. In Spectrum B, there was no Ni-related peak within the limit of XPS analysis, while the atomic concentration of Ni was ~5.8% on the surface before the thermal treatment (see spectrum A). This result indicates that the top-layer Ni atoms were diffused into the a-Si film and induced the Si crystallization during the annealing, although we do not exclude the partial desorption of Ni (or nickel oxide) species from the surface. The inset of Fig. 3 shows the Ni 2p core level spectrum for one Ni(dmamb)_2-H_2O ALD cycle. The spectrum consists of main peaks of Ni 2p1/2 and 2p3/2 and related broad and strong satellites located on the higher binding energy sides. The peak positions of the Ni 2p1/2 core level and the related satellite are located at 857.1 eV and near 862.2 eV (ΔE = 5.1 eV), respectively, referred to the peak position (285 eV) of the C 1s core level due to surface carbon contamination. The main peak positions and relevant shapes were well established previously.14,15 The peak positions and the line shape of the spectrum are very similar to those of Ni(OH)₂, although the detailed XPS spectrum of Ni(OH)₂ state between the molecular-type species on the top-layer surface and the bulk can be different. The formation of Ni(OH)₂ species on the surface is reasonable because of final H_2O reaction in one Ni(dmamb)_2-H_2O ALD cycle and/or the moisture contamination of the sample in air before XPS analysis. After Ar⁺ sputtering (2 min), the peak position of the Ni 2p core level was considerably
shifted to the lower binding energy side and the satellite disappeared, which indicates the formation of Ni silicide phase, i.e., NiSi2.16

Raman spectroscopy was applied to estimate the crystalline characteristics, since Raman information is highly sensitive to the local atomic arrangement and vibrations. The three modes were included to estimate the amorphous and polycrystalline portions of the Ni-induced crystallization in the a-Si thin films: (i) a broad Si-Si transverse optical (TO) mode band centered at around 475.8 cm−1, (ii) the Si-Si mode for crystalline Si located near 520 cm−1, and (iii) additional Raman shifts between 505.5 and 517.3 cm−1, which are attributed to microcrystalline features of Si.17 The current work suggested that a significant fraction of the crystallinity can be attained on a-Si thin films through the ALD deposition of nickel oxide combined with a reducing atmosphere. Noticeably, the crystallized films did not show the equiaxial grains, unlike Si grains processed using laser annealing.18 The nanoscale grain sizes seemed to cause the Raman shift to be split from one crystalline position in the large-grained Si thin films, leading to a higher fraction of the so-called defective peaks found at approximately 516 cm−1. The defective peak was attributed to the local atomic arrangement subjected to the dangling bonds between the adjacent grains whose sizes are of nanoscale magnitude.19 The fraction of the defective regimes can increase by decreasing the grain size of Si.

The measured Raman intensity was deconvoluted in order to determine the relative volume fractions of the respective component: high absorption characteristic in an amorphous phase should be taken into account, compared to that of the crystalline phase (see Fig. 4a).17 The relevant equation is the following

\[ \text{Volume fraction of component } i = \frac{I_i}{I_A + I_y + I_c} \]  

where \( I_i \) is the integrated intensity of component \( i \), \( y \) is the weighting factor due to high absorption in amorphous Si thin films (in this work, \( y = 0.28 \)), and \( I_A \), \( I_y \), and \( I_c \) are the deconvoluted Raman intensities of defective, amorphous, and crystalline components.17

The amorphous, defective, and crystalline volume fractions were independent of the number of Ni cycles applied to ALD, as shown in Fig. 4. The pseudocrystalline volume fraction, composed of the crystalline and defective portions, is estimated to be approximately 90% (see Fig. 4b). The contribution of the defective component is estimated to be near 20%.17 As expected, however, the a-Si thin films did not crystallize without nickel oxide. The presence of nickel oxide provided a driving force in crystallizing the Si crystals through presumably, nickel silicides (NiSi2). Unlike SPC and ELA, metal-induced crystallization promotes a phase change through nickel-silicon compounds, such as NiSi2, since nickel silicide can be found at a very low temperature and the lattice mismatch between Si and NiSi2 is very small (approximately 4%). The high number of NiSi2 crystallites activates the crystallization of amorphous Si thin films at relatively low temperature through a reduction in activation energy from 3.12 eV20 of SPC to 1.5 eV21 of MIC. Otherwise, the conventional SPC requires 20 h at 600°C.5

The deposition of Ni onto a-Si thin films has been performed using evaporation,22 sputtering,23-25 and a Ni-based solution.”26 Those approaches suffered from an inability to control the Ni content. In ALD-mediated crystallization, one single cycle of nickel oxide is high enough to induce crystallization in a-Si: the Ni content was calculated to be approximately 2.3 × 1014 atoms/cm², extrapolated from secondary ion mass spectrometry measurement. The reported Ni concentrations are summarized in Table I. Depending on the preparation methods, the Ni concentrations exhibited a wide variation, i.e., ranging from 4.6 × 1012 to 1.2 × 1016 atoms/cm². The comparison on the Ni concentrations indicates that ALD-mediated crystallization requires further refinement, leading to the minimization of Ni contents through optimization of processing variables or modification of Ni precursors in ALD. In other words, ALD can be manipulated to control the amount of Ni due to the self-limiting growth of Ni- and O-based layers in ALD.

ALD has been applied to the crystallization of a-Si thin films deposited on glass substrates at low temperatures such as 140°C. Even a single cycle of nickel oxide has brought about the crystallization of a-Si thin films during 1 h at 575°C under a reducing atmosphere. The highly sophisticated atomic control in ALD has proven to be a highly effective approach in controlling the concentration of Ni as a precursor for metal-induced crystallization. Furthermore, the minimum amount required for seeding to induce crys-

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**Table I. Summary of Ni concentrations crystallized through Ni-induced crystallization obtained through various Ni preparation techniques.**

<table>
<thead>
<tr>
<th>Ni preparation methods</th>
<th>Ni concentration (atoms/cm²)</th>
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<tr>
<td>ALD</td>
<td>4.2 × 10¹⁴</td>
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<tr>
<td>Ni evaporation</td>
<td>1.2 × 10¹⁶</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>5.1 × 10¹³ ~ 1.26 × 10¹⁴</td>
</tr>
<tr>
<td>RF sputtering</td>
<td>4.6 × 10¹²</td>
</tr>
<tr>
<td>DC magnetron sputtering</td>
<td>4 × 10¹³ ~ 1.3 × 10¹⁵</td>
</tr>
<tr>
<td>Ni-based solution</td>
<td>2.4 × 10¹³</td>
</tr>
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tallization was found to be less than or equal to a single layer of nickel oxide. The critical amount of Ni for the crystallization of a-Si thin films is currently being pursued, which will be reported in a forthcoming publication.

Korea Research Institute of Chemical Technology assisted in meeting the publication costs of this article.

References