In situ spectromicroscopic study of nickel induced lateral crystallization of amorphous silicon thin film using SPESM

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Abstract

Scanning photoelectron spectromicroscopy (SPESM) has been used to study nickel metal induced lateral crystallization (Ni-MILC) of amorphous silicon (a-Si) thin films, produced by in situ annealing of vacuum deposited Ni patterned films on a-Si. The spatial variations in the chemical composition of the Ni-MILC of a-Si were directly imaged. High-resolution photoemission spectra of both Si 2p and Ni 3p core levels and valence band were used to evaluate morphological changes and chemical interactions. Our direct spectromicroscopic characterization clearly shows that the Ni-MILC process in UHV leads to the lower crystallization temperature and a faster crystallization speed of a-Si, and a poly-Si film with high-crystallinity can be obtained. A unified mechanism for the enhanced growth rate of the high-crystallinity poly-Si film produced by Ni-MILC in UHV is proposed.

Keywords: Scanning photoelectron spectromicroscopy; Metal induced lateral crystallization; Polycrystalline silicon; Si 2p core level

1. Introduction

Low temperature polycrystalline silicon (LTPS) technology is the novel technology specific for flat-panel displays, organic light-emitting diodes, solar cells, and so on. Because polycrystalline silicon (poly-Si) thin film transistors (TFTs) should be made on inexpensive glass substrates for the low fabrication cost, it is indispensable to decrease the crystallization temperature of a-Si films as low as possible. The studies showed that metal induced lateral crystallization (MILC) leads to the realization of TFTs at a significantly reduced process temperature with improved characteristics. Therefore, various MILC methods have been proposed to shorten the thermal annealing time and lower the process temperature [1–9]. In a common MILC, a thin metal film is deposited on top of an a-Si film and the latter will crystallize upon annealing. Several metals including Ni [4], Pd [8] and Al [9] are under scrutiny of many research groups to explore their suitability for the application. To date, Ni appears to be one of the best suited metals for MILC. It has been already shown that the Ni-MILC phenomenon is based on the formation of NiSi2 precipitates and their subsequent migration though a-Si film, leaving a trail of crystalline Si grown on the lattice-matched silicides of NiSi2.

Despite the recent progress made towards Ni-MILC of a-Si, an understanding of the chemical reaction involved in Ni-MILC still lacks complete clarity due to the lack of suitable experimental method. In our present study, the lateral chemical variations of a-Si thin film induced by the patterned Ni pads was studied in detail, performing in situ vacuum annealing experiments with SPESM. The spectromicroscopic information on the lateral variations in the local chemistry of the different chemically-shifted phases formed in MILC process was clearly revealed. The Si 2p chemical maps and the Si 2p, Ni 3p and VB spectra...
showed that the Ni-MILC process in UHV leads to the lower crystallization temperature and a faster crystallization speed of a-Si, and a poly-Si film with high-crystallinity was laterally grown over ∼20 μm at 500 °C within 1 h. A unified mechanism for the enhanced growth rate of the high-crystallinity poly-Si film produced by Ni-MILC in UHV is proposed.

2. Experimental

Thin a-Si film of 1000 Å thickness was deposited on a 3000-Å thick oxidized Si wafer by low-pressure chemical vapor deposition (LPCVD) using silane at 550 °C and 300 mTorr. A poly-Si film with 3000 Å thickness was also prepared by LPCVD at 620 °C. Both a-Si and poly-Si films were cleaning with Ar+ ion sputtering. SPESM was used to make certain there was no residual O contamination on a-Si and poly-Si films.

The patterned Ni metallic film was prepared in the UHV chamber connected to the SPESM station, which hosts two OMICRON EF3 water-cooled electron-beam evaporators. The base pressures of both the preparation chamber and SPESM station are 3 × 10⁻¹⁰ Torr and 2 × 10⁻⁹ Torr, respectively. 2-nm thick Ni circle pads were deposited on a-Si film at room temperature (RT). The deposition rate was 20 Å/min. The patterned Ni circle pads were formed by evaporating Ni flux through a mask with pinhole size of ∼70 μm. The pressure during Ni deposition was less than 5 × 10⁻¹⁰ Torr. The Ni silicide was produced by direct-current heating of vacuum deposited Ni films on a-Si substrate. Since electrical current flows in a-Si films, the a-Si film is self-heated by Joule heating. The Joule heat generated at the Ni pads diffuses into the underlying a-Si film and the Ni silicide was formed. The electric current was applied to the specimen by a dc power supply through the molybdenum electrodes formed on two opposite edges of the substrates during crystallization. The crystallization process was performed at 500 °C for 1 h with an electrical current of 300 mA and a bias voltage of 30 V under the pressure of 8 × 10⁻¹⁰ Torr. This crystallization method using electric current-induced Joule heating of silicon has also been reported in previous studies [10–12].

SPESM measurements were carried out at the U5-undulator beamline of National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan [13,14]. A high-efficiency (25%) Ni Fresnel zone plate (ZP) optics was employed to focus a soft X-ray beam onto an 100-nm spot size. The ZP is obtained from Berkeley Lab’s Center for X-ray Optics (CXRO). The photoelectrons emitted from the illuminated microspot were collected by a hemispherical electron energy analyzer with a 16-channel detection scheme. Photoelectron images of the patterned surfaces were obtained by scanning the sample with respect to the photon beam and recording a 16-channel spectrum at every sample position. This resulted in the simultaneous acquisition of 16 SPESM images at 16 different kinetic energies within the energy range covered by the 16-channels (~5 eV for the setting of the present measurement).

![Fig. 1. Chemical state maps (160 × 160 μm²) of different kinetic-energy Si 2p photoelectrons from a Ni circle pad on a-Si, obtained at RT (a) and after in-vacuum heating at 500 °C for 1 h (b), respectively. (c) Si 2p intensity profile taken across the MILC region along the dashed line in (b). Two dashed circles indicate the boundary of A and C regions.](image-url)
The simultaneous acquisition of the 16 different SPEM images is called the method of “Parallel Imaging for Chemical State Mapping” (PICSM) [13,14]. In addition to these “pixel spectra”, conventional micro-XPS (μ-XPS) spectra were taken from selected areas of samples with the focused beam. The valence band and both Si 2p and Ni 3p core levels spectra were recorded with photon energy of 387 eV. The overall instrument resolution is better than 0.2 eV. The sampling depth is about 30 Å for the present experimental setup.

3. Results and discussion

Fig. 1 shows the Si 2p SPESM images (160 × 160 μm²) of Ni circle pad patterned on a-Si film taken at RT (a) and after in situ heating at 500 °C for 1 h (b), respectively. These different chemical state images in Fig. 1 are simultaneously acquired by the PICSM method. The contrast in these chemical state maps reflects the variations in the contents of different chemically-shifted Si phases. After Ni deposition on a-Si at RT, two distinct regions are visible in the image, i.e. the Ni circle pad (region A) was patterned in an a-Si area (region B), as shown in Fig. 1a. Moreover, in the chemical state image taken at 99.55 eV binding energy (BE), an intense Si 2p emission was observed in region A. This indicates that a large amount of the chemically-shifted Si phase at BE of 99.55 eV are formed in region A. As will be demonstrated below, this observation is due to the considerable reactivity of Ni and Si, leading to faster formation of Ni silicides. Upon annealing at 500 °C for 1 h, a bright MILC ring (region C) developed outside region A in the chemical state image at BE of 99.65 eV, shown in Fig. 1b. This bright MILC ring appearing around Ni pad (region A) after annealing is usually seen in the optical micrograph of MILC in the previous papers [2,4]. Uniform chemical composition and morphology were observed in MILC area. Si 2p intensity profile was taken across the MILC region as indicated by the dashed line inside the image at BE of 99.65 eV, and is displayed in Fig. 1c. In Fig. 1c, it was found that the width of the bright ring (region C) is about 22 μm. The annealing time for lateral crystallization over 22 μm in our work (1 h) is very shorter compared with that (20 h) of the previous MILC studies [1–4]. That is, Ni effectively induced lateral crystallization of a-Si over 22 μm in our work. The reason that causes the faster crystallization speed will be explained below.

Fig. 2a shows the corresponding Ni 3p map (160 × 160 μm²) taken after annealing. The Ni covered area (region A) still appeared brighter in the Ni 3p image. In order to see the lateral distribution of Ni concentration, a Ni 3p intensity profile measured along the dashed line in Fig. 2a is displayed in Fig. 2b. The Si 2p intensity profile of Fig. 1c is also overlaid on the Ni 3p intensity profile. Referring from Figs. 1c and 2b, besides a ~6 μm wide diffusion zone close to region A, no trace of Ni 3p signal was detected inside the C area, in agreement with the result of Auger Electron Spectroscopy (AES) analysis reported by Jin et al. [2]. However, since the size of NiSi₂ precipitates at the crystallization front is less than 100 nm [1,15–17], so that the Ni concentration of NiSi₂ precipitates at the crystallization front is too low to be detected by Energy Dispersive X-ray (EDX) analysis [18,19]. And the detection sensitivity of SPESM is below that of EDX. That is, the Ni concentration of NiSi₂ precipitates is below the detection limit of SPESM. Thus, no Ni 3p signal can be detected at the crystallization front in our Ni 3p map. By the same reason, the Si 2p signal of NiSi₂ phase cannot be obtained at the crystallization front in Si 2p chemical state image.
Fig. 3 displays the high-resolution μ-XPS of Si 2p core level spectra (a, b) and corresponding valence band spectra (c, d), measured from different regions of Ni circle pad on a-Si as indicated in Fig. 1. In addition, Fig. 3a, c and b, d also present the RT sample and the annealed sample, respectively. The bottom spectrum in Fig. 3a plots a broader and structureless Si 2p lineshape from the a-Si area (region B) and shows the main peak position at 99.97 eV. The broadening of Si 2p core level of a-Si is attributed to the variation in valence charges due to disorder in the a-Si film [20]. A strong and wider Si 2p peak from region A is observed at 99.58 eV in Fig. 3a, indicative of coexistence of various phases. This suggests that under UHV the deposited Ni atoms penetrate the a-Si substrate even at RT and react strongly with Si atoms, forming a Ni-rich amorphous silicide [21]. As shown in Fig. 3c, the Ni 3d BE in the valence spectrum taken from region A is at 1.6 eV, close to the position of Ni 3d states for Ni$_2$Si at 1.3 eV [22]. In the same area the Ni 3p position in Fig. 4a is at 65.33 eV, in agreement with Ni 3p BE for Ni$_2$Si [22]. Therefore, our results indicate that an amorphous Ni$_2$Si layer was immediately formed when Ni was deposited on a-Si at RT under the pressure of $5 \times 10^{-10}$ Torr. Our observation is different from the previous studies by Jang [1], who reported that Ni$_2$Si was formed at 150 °C. This means that the strong chemical reaction of Ni and a-Si at RT in UHV leads to reduce the crystallization temperature of silicides.

The shape of Si 2p spectrum from region A in Fig. 3b shows two closely spaced peaks with 0.43-eV separation and their leading Si 2p peak is chemically shifted toward a lower BE at 99.34 eV. This negative energy shift indicates that Ni continues to penetrate the a-Si substrate to form a Si-rich silicide after 500 °C annealing [22]. In region A, the two obvious resolvable doublets of Si 2p core level observed after annealing is certainly different from the broader Si 2p line shape taken at RT deposition. Thus, these two well-resolvable doublets of Si 2p core level from region A are indicative of the formation of epitaxial Ni silicide film. In Fig. 3d, the Ni 3d position taken from region A is at 2.2 eV, typical of the NiSi phase [22]. Also, the BE of Ni 3p core electrons from A region in Fig. 4b is at 65.62 eV, close to the Ni 3p position of NiSi [22]. Thus, these photoemission spectra of both Si 2p and Ni 3p core levels as well as valence bands, from region A, strongly suggest that an amorphous Ni$_2$Si layer became an epitaxial NiSi film after MILC process in UHV.

In Fig. 3b, it is interesting to note that two closely spaced peaks in Si 2p spectrum from region C is clearly resolvable with 0.6 eV, similar to the characteristic Si 2p spin-orbital (SO) splitting of single-crystalline Si [23]. It is certainly different from the Si 2p line shapes of poly-Si film obtained by Wesner and Eberhurdt [20] and our clean LPCVD poly-Si (in Fig. 5). The main peak of Si 2p position is at 99.62 eV. Moreover, no Ni 3p intensity was detected at region C, as shown in Fig. 4b. And, as seen in Fig. 3d, no Ni 3d states were observed in the valence band spectrum. Only three broad peaks remained in the valence band spectrum, which originate primarily from the pure Si
phase (i.e. Si 3s, 3sp, and 3p states) [20,24]. Also, the intensities of these states are stronger than that of LPCVD poly-Si film, shown in the bottom spectrum in Fig. 3d. As reported by Thorp and Weaire [25], the emissions near the top of valence band of Si film are sensitive to long-range order. Our spectrum from region C is in agreement with this picture. According to these results, we speculate that a poly-Si film with high-crystallinity is formed after MILC process in UHV. The further demonstration is shown in our other paper [26], in which the peak fittings of Si 2p spectra from both regions of A and C areas were performed to identify the chemical bonding of different chemically-shifted Si 2p components. Based on the assignments of peak fitting, we have certified that the two closely spaced peaks in Si 2p spectrum from region C indeed originates from the 0.6-eV SO splitting of Si 2p core level of single-crystalline Si. We hereafter denote this high-crystallinity poly-Si film as C-Si.

The shapes of both Si 2p core level and valence band spectra from region B taken after annealing are very similar to those taken before annealing. The only notable difference between the two Si 2p spectra of area B at various heating conditions is a small bump on the high BE side of Si 2p peak of the annealed a-Si, as shown in the insert of Fig. 3b. This feature should originate from the suboxides phase. As for the comparison between the two valence band spectra of area B at various heating conditions, we only can find that the valence-state intensity of the annealed a-Si is lower than that of the RT a-Si, as displayed in the insert of Fig. 3d. This may be due to the slight contamination on the annealed a-Si during SPESM measurement. The band offset between C-Si and a-Si is about 0.52 eV, which was determined from the spacing of their valence-band maxima (VBM) of the spectra in Fig. 3d. The position of the VBM as defined here is indicated by extrapolations of the leading edge to the base line.

The comparisons of the Si 2p line shapes of C-Si, poly-Si, and a-Si are displayed in Fig. 5. The line shape of clean LPCVD poly-Si was taken after annealing at 950 for 10 min, but its SO splitting is not as clear as that of C-Si. Thus, the clearly resolved SO splitting of Si 2p core level of C-Si means that an epitaxial poly-Si film was formed, and its crystalline structure may be almost single crystalline, not a textured structure.

Fig. 6 schematically illustrates the model we propose for the mechanism of MILC process in UHV, which is account for our experimental results. Under the pressure less than $1 \times 10^{-9}$ Torr, Ni is not stabilized on a-Si and has high

![Fig. 4](image1.png)  
**Fig. 4.** μ-XPS of Ni 3p core-level spectra from different regions of A, B, and C that indicated in Fig. 1.

![Fig. 5](image2.png)  
**Fig. 5.** μ-XPS of Si 2p core-level spectra of C-Si, poly-Si, and a-Si.
diffusivity and high solubility in a-Si even at RT, which could potentially result in Ni precipitates that act as shunts. The reaction with a-Si substrate has completely consumed the Ni film yielding an amorphous Ni$_2$Si layer (see Fig. 3a and c). Then annealing of Ni$_2$Si layer with higher temperature at 500 °C, it naturally can cause depletion of Ni$_2$Si layer to form an epitaxial NiSi pad in the early stage of thermal annealing (see Fig. 3b and d). This is because 500 °C is high enough for the formation and grain growth as well as grain coalescence of NiSi. With direct-current heating at 500 °C, it is possible to cause Ni atoms in the surrounding region of the NiSi pad laterally diffuse to a-Si and lead to form small NiSi$_2$ crystallites with the size less than 100 nm [1,15,16]. Then, by the migration of NiSi$_2$ crystallites into the a-Si, the a-Si can be gradually crystallized. Since NiSi$_2$ acts as a template for the Si crystallization, if the NiSi$_2$ itself is single crystalline, a high-crystallinity poly-Si film will be the result of the MILC process. However, due to the Ni concentration of NiSi$_2$ precipitates below the detection limit of SPESM, the NiSi$_2$ nano-crystallites cannot be detected by SPESM. But, according to our results, the Ni as-deposited pad becomes an epitaxial NiSi film after annealing at 500 °C for 1 h in UHV. Therefore, it is possible that the surrounding region of NiSi film can be converted to single-crystalline NiSi$_2$ film [27]. And the direct-current heating enhances the migration speed of NiSi$_2$ in the presence of an electric field [7,10–12]. This leads to the fast crystallization speed of a-Si via the accelerated migration of the NiSi$_2$ precipitates through the a-Si. Thus, the a-Si is crystallized laterally over ~20 μm at 500 °C within 1 h. And an epitaxial poly-Si film with fairly high-crystallinity can be obtained by the Ni-MILC process in UHV (see Fig. 5).

4. Summary

In summary, we have exploited in situ SPESM to monitor morphological changes and chemical interaction of the Ni circle pads patterned on a-Si film during MILC process in UHV. With chemical and spatial sensitivity on the sub-micrometer scale, the lateral distribution of variations in chemical bonding for the different chemical phases formed in MILC process were directly revealed. Via a system study of the correlation between the core and valence level spectra, our results show clearly that the UHV condition enhances the chemical reaction of Ni atoms and a-Si and then leads to reduce the crystallization temperature. With the direct-current heating in UHV, the crystallization speed of a-Si increases via the accelerated migration of the NiSi$_2$ precipitates through the a-Si in the presence of electric filed. Therefore, after annealing at 500 °C for 1 h in UHV, a 0.6-eV SO splitting of the Si 2p levels is clearly observed at the MILC area, which indicates the transformation of a-Si film to an epitaxial poly-Si film with fairly high-crystallinity.

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