Classification of metals inducing field aided lateral crystallization (FALC) of amorphous silicon

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Abstract The effects of various metals on Field Aided Lateral Crystallization (FALC) behaviors of amorphous silicon (a-Si) were investigated. Under an influence of electric field, metals such as Cu, Ni and Co were found to fasten the lateral crystallization toward a metal-free region, exhibiting a typical FALC behavior while the lateral crystallization of a-Si was not obvious for Pd. However, Au, Al and Cr did not induce the lateral crystallization of a-Si in metal-free region. Such phenomenological differences in various metals were studied in terms of dominant diffusing species (DDS) in the reaction between metal and Si. It was judged that the applied electric field enhanced the crystallization velocity by accelerating the diffusion of metal atoms since the occurrence of lateral crystallization would be strongly dependent on the diffusion of metal atoms than that of Si atoms. Therefore, it was concluded that the only metal-dominant diffusing species in the reaction between metal and Si results in the crystallization of a-Si in metal-free region.

1. Introduction

High mobility polycrystalline silicon thin film transistor (poly-Si TFTs) with low leakage currents is desirable for integrating driver circuits and pixel transistors on the same glass panel for active matrix liquid crystal displays (AMLCDs) to achieve high definition and fast response time. As a result, a number of poly-Si formation techniques have been developed during the past several years. However, one of the most essential issues in poly-Si formation is to reduce the crystallization temperature of a-Si in order to realize a system on glass substrate for commercial applications. Recently, a low-temperature (< 500°C) crystallization using the effect of metal impurities on the crystallization of a-Si has been proposed [1]. For example, metal induced crystallization (MIC) using such metals as Al, Au, Co, Cu, Ni and Pd can be used to lower the crystallization temperature, along with formation of the silicide phase or alloy in the reaction with Si. In addition, the selective deposition of palladium (Pd) or nickel (Ni) thin films on a-Si has been reported to induce crystallization of a-Si in metal-free region [2, 3]. This crystallization method, metal induced lateral crystallization (MILC), is known to be mostly mediated by

the metal silicide phase formed at the interface between crystalline silicon (c-Si) and a-Si [4]. However, it has shortcomings of relatively long crystallization time and metal contamination at the center of the transistor channel region.

Therefore, we proposed a novel concept of crystallization technique, field aided lateral crystallization (FALC), in which the crystallization is more enhanced and the crystallization time can be shortened [5, 6]. In previous works, we have investigated the FALC characteristics and could successfully fabricate the poly-Si TFT using Ni-FALC [6, 7] at a temperature as low as 500°C and have checked diverse crystallization aspects using Cu-FALC [8].

In this study, we have tried to examine the FALC behaviors and investigate the differences in the crystallization aspects for various metals. Besides Ni and Cu, we used metals such as Au, Al, Co, Pd as a crystallization mediator, which are known to form a silicide phase or an alloy with Si and induce the MIC. Meanwhile, the silicide phase, which is formed in the reaction between metal and Si, is known to mediate the formation of poly-Si in the MIC process. For Ni, the silicide phase, NiSi₂, which has 0.4 % lattice mismatch with <111> direction of Si, is reported to grow epitaxially on single c-Si [9]. Based on this report, we tested the possibility of lateral crystallization of Cr in the presence of electric field because Cr silicide has no lattice mismatch with <111> direction of Si [10].

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Finally, we attempted to interpret the FALC mechanism in terms of dominant diffusing species in the reaction between metal and Si.

2. Experimental Procedure

P-type (100) silicon wafers covered with 500 nm-thick thermal oxide were used as the starting substrates. A thin 100 nm a-Si layer was deposited by plasma enhanced chemical deposition (PECVD) at 300°C using Si_2H_6 as a source gas and then cut into $2.5\times2.5\,\text{cm}^2$ square samples. Photoresist (PR) was patterned by a photolithographic process to selectively deposit thin metal layer on a-Si thin films. T-shaped mask patterns with various widths from 5 mm to 120 μm were used. After thin metal layer (Al, Au, Co, Cr, Cu, Ni and Pd), below 5 nm, was deposited by DC sputtering system, the metal on the PR were removed by lift-off process and thin metal layer on the a-Si outside of patterns were left.

Electric field was applied to the selectively metal-deposited specimen by DC power supply during thermal annealing after the electrodes were formed using silver paste on two opposite sides of the specimen. Electric field was calculated from dividing the applied voltage by the distances between two electrodes. A schematic diagram of the prepared specimen for FALC process is shown in Fig. 1. The crystallization process was carried out at various annealing conditions in N₂ ambient. After the heat treatment, the crystallization behavior and the lateral crystallization velocity in

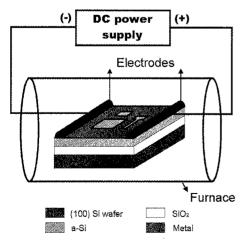


Fig. 1. A schematic diagram of the prepared specimen for FALC process.

every pattern of specimen were identified by Nomarski optical microscopy. FALC velocity was calculated from dividing the progressed crystallization distance in pattern by annealing time. The degree of crystallization was estimated by Raman spectroscopy. The laser of 515 nm wavelength was used and its diameter was in the range of 5 μ m and 100 μ m.

3. Results and Discussion

Nomarski optical micrographs of partially crystallized a-Si using Cu, Ni, Co and Pd in the presence of electric field is shown in Fig. 2. In the case of Cu (Fig. 2(a)), the crystallization of a-Si occurred not only at the Cu-deposited region outside of T pattern but also at the Cu-free region, inside of T pattern during the thermal annealing at 500°C for 3 hrs with an electric field of 2.1 V/cm. The lateral crystallization of all the Cu-deposited patterns was remarkably accelerated at the negative electrode side compared to the positive electrode side, which exhibits a typical FALC aspect. But, the leading front of crystallization was not parallel to the negative electrode. This is caused by the fact that lateral crystallization progresses faster at the corner than the center of the pattern in the absence of electric field and the lateral crystallization toward metal-free region proceeds in the direction perpendicu-

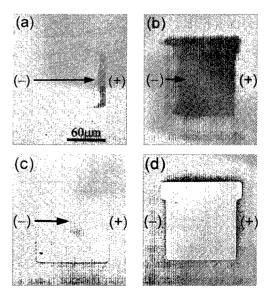
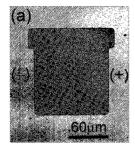
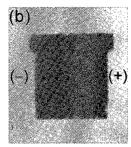


Fig. 2. Nomarski optical micrographs of the partially crystallized a-Si using (a) Cu, (b) Ni, (c) Co and (d) Pd by electric field, respectively.





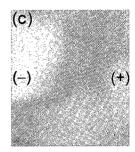


Fig. 3. Nomarski optical micrographs of the crystallized a-Si at 500°C for 3 hrs with an electric field of 2 V/cm using (a) Al, (b) Au and (c) Cr, respectively.

lar to the electrode by electric field. So, the lateral crystallization velocity has different values in every pattern and the center of leading front has the slowest crystallization velocity. In the left-hand side of inside of T pattern, the FALC velocity was approximately $35\,\mu\text{m/h}$, which is much faster than the case without electric field.

For the FALC using Ni, the distinct crystallization behavior (Fig. 2(b)) was observed in comparison with the case of Cu. Although the lateral crystallization under the electric field proceeded in the direction perpendicular to the edge of negative electrode, the fastest crystallization occurred not at the corner but at the center of pattern, which is opposite to the case of Cu. Electric field of 2.1 V/cm was applied to the selectively Ni-deposited specimen during the heat treatment at 500° C for 3 hrs and the Ni-FALC velocity was approximately $9.5 \ \mu m/h$.

For Co (Fig. 2(c)), the lateral crystallization by electric field was also clear as in the case of Cu and Ni, exhibiting the directional crystallization from negative electrode side toward positive electrode side. The crystallization using Co, however, occurred at as high as 600°C for 1 hr with an electric field of 2.8 V/cm. This is associated with the Co silicide formation temperature, which is known to be above 550°C. Although the crystallization of a-Si can be accomplished by thermal annealing above 600°C without the aid of metal impurities, the crystallization velocity of a-Si using Co can be drastically enhanced with an aid of electric field.

In Pd-induced crystallization (Fig. 2(d)), the lateral crystallization is not obvious under the applied bias. Because the lateral crystallization by Pd leads to the formation of needle-like structure, the exact measurement of progressed crystallization distance is not easy in the partially crystallized region. Compared with the case in the absence of electric field (MILC), the progress of crystallization appeared to be rather decreased

for applying the electric field of 2.1 V/cm at 500°C for 3 hrs

Figure 3 shows the Nomarski optical micrographs of specimen after crystallization using (a) Al, (b) Au and (c) Cr. In this case, the electric field of 2 V/cm was applied to the specimen at 500°C for 3 hrs. Generally, Al and Au were reported to induce low-temperature crystallization in the metal-contacted a-Si area at 170°C [11] and 130°C [12], respectively. However, it was found that these metals could not induce the lateral crystallization toward the metal-free region in the presence of electric field as shown in Fig. 3(a) and (b). For Cr, the effect of electric field on the lateral crystallization of a-Si as well as Cr induced crystallization of a-Si was not identified. In other words, there is no evidence of metal induced crystallization and lateral crystallization by electric field (Fig. 3(c)).

Raman beam was focused on the crystallized region

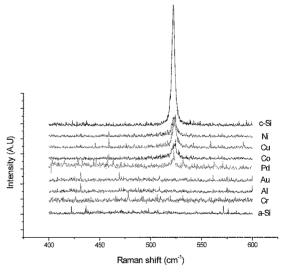


Fig. 4. Raman spectra for various metals under the influence of electric field.

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Dominant	diffusing	species in	the	reaction	with	Si for	various	metals	3
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Metal	MIC	MILC	FALC	DDS in the reaction between metal and Si	FALC temp. $(^{\circ}C)$	Ref.
Cu	0	0	0	Cu	≤ 500	13
Ni	0	0	0	Ni	≤ 500	14
Co	0	0	0	Co	≥ 600	15
Pd	0	0	\times	Pd and Si	_	. 16
Al	0	×	\times	Si	-	17
Au	0	×	\times	Si	-	18
Cr	×	×	×	Si	-	19

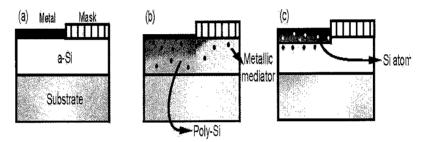


Fig. 5. Schematic diagrams of lateral crystallization model. In the reaction between metal and Si, (a) as-deposited, dominant diffusing species are (b) metal and (c) Si.

inside of the pattern in order to measure the degree of crystallization. Single c-Si has a sharp peak around 520 cm⁻¹ in Raman spectra (Fig. 4). The intensity of Raman spectra measured from the partially crystallized region, inside of pattern by using Cu, Ni, Co and Pd does not reach the intensity of single c-Si but it shows the obvious evidence of crystallization. However, the characteristic peak of c-Si in Raman spectra was not observed in the metal-free region for Al, Au and Cr. Additionally, there are no big differences in Raman spectra results in comparison with a-Si. From these results, Cu, Ni and Co were found to induce the lateral crystallization by applying an electric field while Al, Au and Cr could not induce the lateral crystallization of a-Si by electric field.

The crystallization behaviors for various metals are summarized in Table 1. It is interesting to note a report by Hayzelden *et al.* [4] where the crystallization is greatly mediated by the metal silicide phase. Concerning his report, it is understandable that the metals, which form a silicide phase, such as Cu, Ni can induce lateral crystallization. However, the lateral crystallization phenomenon did not occur for Cr, which has been known to form a silicide. This may result from the difference in the silicide formation mechanism, nucleation in the case of Cr. Also, it was revealed that

Au did not induce the lateral crystallization even though it formed a meta-stable silicide phase. Based on above observations, it is thought that the formation of silicide phase is not a sufficient condition for the lateral crystallization of a-Si.

Considering the required conditions for the occurrence of lateral crystallization by an electric field, the crystallization toward metal-free region (MILC) has to occur by thermal annealing in the absence of electric field as shown in Table 1. Up to date, the most widely accepted model of lateral crystallization of a-Si using metals (Fig. 5) is that metal and Si atoms diffuse, react and form silicide phase and then it mediates the crystallization of a-Si. That is, the lateral crystallization is related to the migration of silicide phase. For crystallization mechanism of a-Si using Ni, for example, it is reported that NiSi2 phase acts as a crystallization mediator. This silicide, then, moves into the a-Si for the further crystallization. Hayzelden et al. [4] reported that the chemical activity difference of either Ni or Si atoms at the boundaries between silicide/a-Si and silicide/c-Si is the driving force for the migration of silicide precipitate.

If the dominant diffusing species (DDS) is metal in metal-Si system, the migration of metal atoms into uncrystallized a-Si is more feasible than the reverse case. Then the electric field can somehow enhance the diffusivity of metal atoms, which leads to fast and directional crystallization. Figure 5(b) shows a schematic diagram of lateral crystallization model in case that the DDS is metal. Cu, which forms a silicide, Cu₃Si [13], is known to be DDS in metal-Si system. For this reason, the Cu diffuses into a-Si and the crystallization can proceed toward inside of the pattern where Cu atoms are not in contact with Si. Ni and Co are also DDS in metal-Si system so that they can induce the lateral crystallization of a-Si. However, the effect of electric field on the lateral crystallization is not obvious for Pd because both Pd and Si is known to be DDS in Pd-Si system.

On the other hand, if the DDS is Si (Fig. 5 (c)), Si atoms would preferentially diffuse into metal layer leaving vacant sites, which are subsequently replaced by metal atoms. In case of a very thin layer of metal (<5 nm), such replacement stops soon after the reaction and the most metal atoms reside where originally deposited. Then the further migration of metal atoms into metal-free region, which is possible by diffusion of Si atoms, will be impossible. That is, since the formation of poly-Si strongly relies on the diffusion of metal into a-Si, the progress of lateral crystallization using these metals is not quite available and the crystallization would be restricted to metal-Si contacted area only. Metals like Au, Al and Cr are classified into this category.

From above consideration, the FALC mechanism can be elucidated as follows. In order for FALC to occur, it is required that metals have to induce the crystallization toward metal-free area. And this is possible only when these metals are DDS in metal-Si system. In this case, metals diffuse into Si and react with Si. Therefore, it is thought that the applied electric field during the heat treatment can play a crucial role in enhancing driving force to migrate metal atoms. As a consequence, the crystallization of a-Si occurs not only at metal-contacted region but also in metal-free region with a more enhanced crystallization velocity with an aid of electric field.

4. Conclusions

Under an influence of electric field, Cu, Ni and Co induce the lateral crystallization of a-Si, showing a typical FALC behavior from negative electrode side toward positive electrode side while the lateral crystal-

lization of a-Si toward metal-free region is not obvious for the case of Pd. On the other hand, the lateral crystallization caused by electric field is not observed for Al, Au and Cr. These phenomenological differences for various selected metals are related to the DDS in the reaction with Si. It is thought that because the lateral crystallization by electric field would mainly be dependent on the diffusion of metal atoms than that of Si atoms, the crystallization velocity could be more improved by accelerating the diffusion of metal atoms with an aid of electric field. Therefore, it is judged that the only metal-dominant diffusing species in the reaction between metal and Si could strongly affect the crystallization of a-Si in metal-free region in the presence of electric field.

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