Extended Abstracts of the 1995 International Conference on Solid State Devices and Materials, Osaka, 1995, pp. 902-904

New Crystallization Process of LPCVD a-Si Films below 530°C Using Metal Adsorption Method

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A new process for low-temperature crystallization of a-Si film was proposed. Several metals were adsorbed on LPCVD a-Si films by spin-coating of metal solutions and the films were successively annealed in Ar atmosphere. The a-Si films adsorbed by Cu and Au among the various metals were completely crystallized below 530℃ within 20 hours. The field effect mobility of the poly-Si TFTs fabricated using the annealed Si films with various Cu adsorption was 6～10 ㎠/V·s before hydrogen passivation.

1. Introduction

Polycrystalline silicon (poly-Si) thin-film transistor (TFT) has received much attention for its wide range of applicability in large area electronics, such as in the active matrix liquid crystal display (AMLCD) with peripheral driving circuits[1]. Poly-Si TFTs are applied to smaller and higher resolution LCDs while amorphous silicon (a-Si) TFTs are aimed at larger displays such as 10" LCDs. Because a-Si TFTs are limited by high defect density and low yield[2]. One of the common methods preparing poly-Si film is solid phase crystallization (SPC) of a-Si film at 600℃ for many tens of hours[3]. But to retain the integrity of the low cost glass substrate, the SPC anneal has been limited to 500℃ or less. The studies of the interaction between a-Si layer and metal layers show that crystallization of a-Si occurs at lower temperature as compared with the isolated a-Si layer. By using metal-Si eutectic temperature, a-Si film can be crystallized below 500℃[4,5]. But in that case the film forms silicide or alloy, which is not applicable to channel layer of TFTs. In this work, we propose a new process, which lowers crystallization temperature and reduces crystallization time. The annealed films by this new process may be adopted as channel layer of TFTs.

2. Experimental

Amorphous Si films of 150 nm thickness were deposited on thermally oxidized Si substrates by low-pressure chemical vapor deposition (LPCVD) at 540℃ using 100% silane (SiH_4) gas. The thickness of the thermal oxide on Si was 750 nm. Several metals such as Au, Cu, Ag, Zn, Fe, Cr and Al were adsorbed on the a-Si films by spin-coating of metal solutions with various concentrations after cleaning by H_2SO_4 + H_2O_2 and 50:1 HF. The all metal solutions were commonly used standard solutions. For example, the Cu concentration in solution is controlled by adding $CuCl_2$. Successively the metal-adsorbed a-Si films were annealed in Ar atmosphere. Relative amount of metal to Si in the annealed Si film was measured by secondary ion mass spectroscopy (SIMS) using a cesium ion gun. Crystallinity was evaluated from thin film X-ray diffraction (XRD) patterns. N-channel poly-Si TFTs with a coplanar structure were fabricated on thermally oxidized Si substrates. After annealing a-Si films, active islands were defined and then a gate insulator 80 nm of SiO_2 was deposited by LPCVD at 470℃. After that, a 350 nm LPCVD poly-Si gate layer was deposited. After defining gate layers, source/drain regions were formed by phosphorous implantation. Then, 500 nm dielectric layer was deposited and densified at 600℃, which also activated the implanted dopant. Contact holes were opened and then Al alloy was evaporated and patterned. The wafers were sintered at 425℃ in a H_2/N_2 atmosphere.

3. Results and discussion

Figure 1 shows the XRD patterns of the Si films annealed at 530℃ for 20 hours with various metals. The films adsorbed with Cu and Au readily crystallized with (111) preferred orientation, while the films adsorbed with other elements did not crystallize

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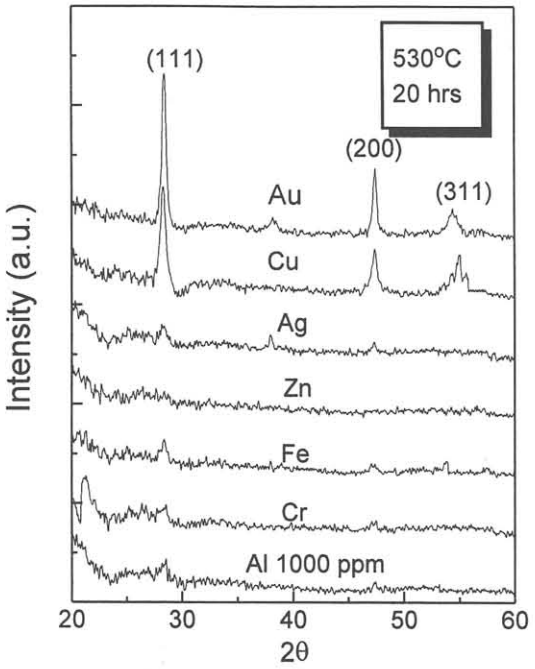

Fig. 1. Typical XRD patterns of the Si films annealed at 530℃ for 20 hours with various metal adsorptions.

readily. Al and Ag are known as crystallization promoting elements of a-Si film when they are deposited as a metal layer on a-Si film. But in this experiment, Al and Au seemed not good promoters for crystallization compared to Cu and Au. The enhancement of crystallization by Cu and Au can be deduced by several factors, such as diffusion length, eutectic temperature and electronegativity. Those factors are summarized table 1. The first two columns are calculated diffusion length of each element in bulk Si for 10 and 20 hours at 530℃. The third and fourth columns are the eutectic temperatures of metal-Si binary system and the electronegativities of metals. First of all, to adsorb more metal molecules on a-Si surfaces, the electronegativity must be larger than 1.8 that is the electronegativity of Si. Ohmi et al have reported that metals such as Cu, which exhibit higher electronegativity than Si in solutions, are adsorbed directly on Si surface by taking electron from Si.[6] And then to enhance nucleation and growth of crystalliztion, the eutectic temperature must be low and diffusion length be long as possible. A few papers are reported that the crystallization temperature of a-Si/metal multilayer is proportional to the eutectic temperature of Si-metal binary system[4,5]. Apparently, Cu and Au satisfy all these conditions.

Table 1. Physical data of metals in Si
(Te:Eutectic temperature, X:electronegativity)

	530℃ 10hr $\bar{x}$ (cm)	530℃ 20hr $\bar{x}$(cm)	Te (℃)	X
Cu	**2.8×10^{-2}**	**3.9×10^{-2}**	**802**	**1.9**
Au	**1.9×10^{-3}**	**2.7×10^{-3}**	**363**	**2.4**
Ag	8.1×10^{-5}	1.1×10^{-4}	835	1.9
Fe	2.8×10^{-2}	3.9×10^{-2}	1207	1.8
Ni	6.6×10^{-5}	9.3×10^{-5}	966	1.8
Cr	1.4×10^{-2}	1.9×10^{-2}	1305	-
Zn	2.0×10^{-3}	2.8×10^{-3}	419	1.6
Al	5.2×10^{-8}	7.3×10^{-8}	577	1.5

Figure 2 shows the (111) XRD intensity and the relative amount of Cu to Si by SIMS of the films, adsorbed with 10, 100, 500 and 1000 ppm of Cu solution and annealed at 530℃ for 20 hours. Below 100 ppm of Cu solution, the a-Si films crystallize too slowly. And the relative amount of Cu to Si in the annealed film is lower than detectable limit of SIMS. On the other hand, the films adsorbed from more than 500 ppm solutions mostly crystallize. Note that the Cu/Si ratio in the films increases rapidly when Cu concentration is above 500ppm. The results clearly show that Cu enhances the crystallization of a-Si films.

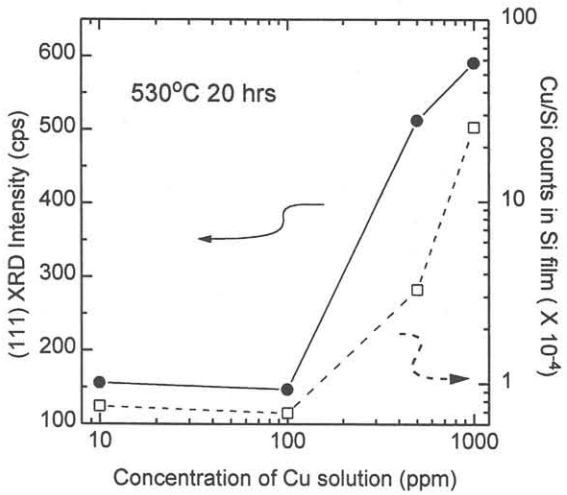

Fig. 2. (111) XRD intensity and the relative amount of Cu to Si by SIMS of the films, adsorbed with various concentrations of Cu solution

Figure 3 shows the SEM surface micrographs of the crystallized film, adsorbed with 500 ppm Cu and annealed at 530℃ for 1, 5, 10 and 20 hours. The number of crystallite fractals seems almost fixed at the initial nucleation stage. The nucleation of crystallites nearly completed within one hour of annealing, indicating that the adsorbed Cu clearly promotes nucleation rate. The size of the crystallite fractals is about 50 ㎛ within 10 hours and the growth rate is 5 ㎛/h, indicating that the adsorbed Cu also enhances growth rate. The exact interaction mechanism between the adsorbed Cu atoms and a-Si

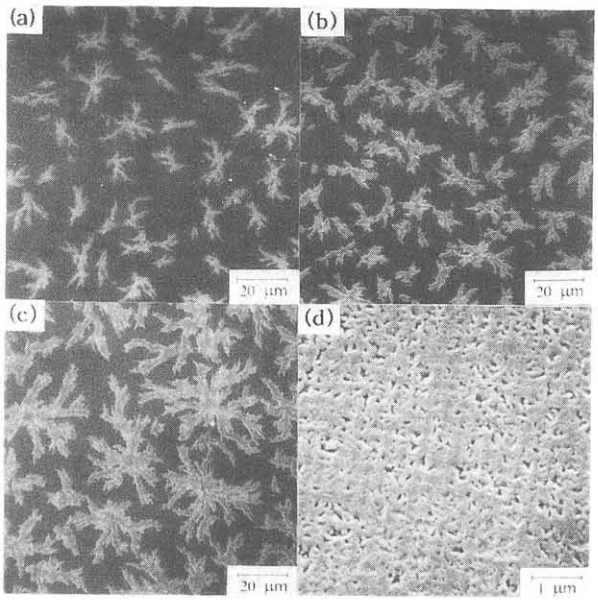

Fig. 3. Plane view SEM photographs of the crystallized film adsorbed with 500 ppm Cu annealed at 530℃ for (a) 1 (b) 5 (c) 10 and (d) 20 hours.

atoms is not known yet.

To investigate the applicability of the crystallized Si films, we fabricated n-channel TFTs on the annealed films. Figure 4 shows the I_D-V_G characteristics of TFTs using the annealed films with 1000 ppm Cu adsorption and without Cu adsorption before hydrogenation. The I_D-V_G characteristics of both TFTs are almost the same. The threshold voltage and the subthreshold slope of the TFTs are 11.2V and about 2.2 V/decade, respectively. Figure 5 shows the field effect mobility versus gate voltage for the TFTs. The field effect mobility was determined from the transconductance measurements at a drain voltage of 0.1 V. As the gate voltage increases, the field effect mobility of the TFT without Cu adsorption continuously increases. On the other hand, that of the TFT with Cu adsorption(1000 ppm) shows a maximum value and then decreases with further increase in the gate voltage. The field effect mobility of TFT without Cu adsorption is about 10 ㎠/V·s at V_G=25V. The mobility is degraded with further adsorption of Cu. It is supposed that impurity scattering is increased by Cu atoms.

4. Conclusions

We proposed a simple new process which lowered SPC temperature and reduced the crystallization time. Consequently, the possibility of using glass substrate is increased. By adsorbing Cu and Au on LPCVD a-Si films, the films were completely crystallized at 530℃ within 20 hours, which temperature is well below the commonly employed SPC temperature (600℃). The characteristics of TFTs fabricated using the films with Cu adsorption are similar to those of TFTs without Cu adsorption, except field effect mobility.

5. References

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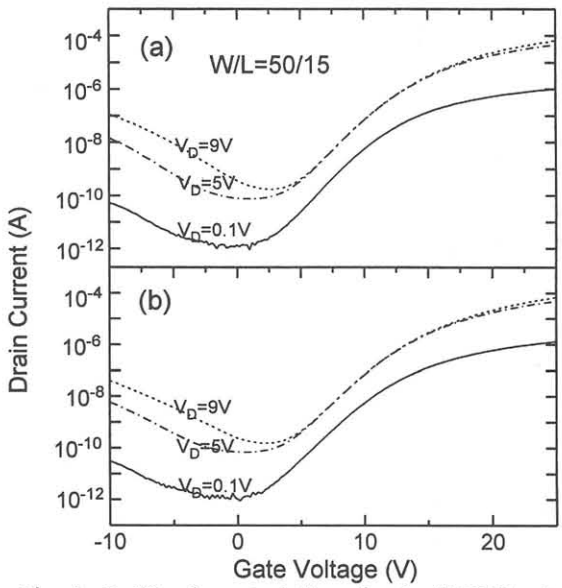

Fig. 4. I_D-V_G characteristics of poly-Si TFT using the annealed Si films adsorbed (a) with 1000 ppm and (b) without Cu.

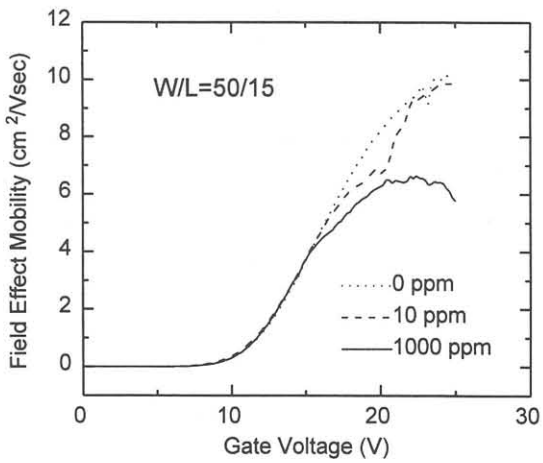

Fig. 5. Field effect mobility versus gate voltage with various concentration of Cu adsorption.