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Metal induced crystallization: Gold versus aluminium

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In this work metal induced crystallization was studied using aluminium and gold deposited over 150 nm amorphous silicon films grown by LPCVD. Aluminium and gold layers with thickness between 1 and 5 nm were deposited on the silicon films and after that, the samples were annealed at 500°C from 5 up to 30 h. When the crystallization is induced through a gold layer, the Si crystalline fraction is higher than when using aluminium. For samples crystallized for 30 h at 500°C with 2 nm of metal a crystalline fraction of 57.5% was achieved using gold and only 38.7% when using aluminium.

1. Introduction

The application of low temperature polycrystalline silicon (poly-Si) to solar cells is being considered aiming the production of active layers, doped layers and/or incubation layers. The conventional way to obtain poly-Si is by low-pressure chemical vapour deposition (LPCVD) that requires high process temperatures on the order of 600–650°C. So, it is important to reduce the temperature needed to get poly-Si films in order to allow the production of devices on low cost substrates such as glass [1, 2]. On the other hand it is known that crystallized amorphous silicon (a-Si) normally presents better electrical properties than as deposited poly-Si. One of the most implemented techniques of obtain poly-Si from a-Si is by Solid Phase Crystallization (SPC) [3]. However on this process the crystallization temperature is too high and the time required for full crystallization is too long. So, lowering the crystallization temperature of a-Si is an important point concerning the application of this material on devices. Metal Induced Crystallization (MIC) [4] appears as a promising solution, presenting some advantages over other crystallization techniques like Excimer Laser Annealing such as lower cost and uniformity over large areas.

Even the metal contamination inherent to this process is not a problem when applying it to solar cells since these films can be used as doped layer and/or incubation layer instead of active layer [5]. In the MIC process, the interaction between certain metals and a-Si induce the crystallization of the silicon at a temperature below that of its intrinsic crystallization temperature (∼600°C). The reaction occurs at the interlayer by diffusion and the driving force for the crystallization of a-Si is the difference in the free energy between amorphous and crystalline phases. The metals used can be classified in two groups: silicide forming metals, such as Ni and Pd, and elemental metals that do not form silicides, such as Al and Au. The aim of this work is to study the differences on the crystallization process of the a-Si when using two metals that do not form silicides: Al and Au.

2. Experimental details

The a-Si samples with about 150 nm were deposited on a tubular LPCVD Tempress Omega Junior furnace on glass (Corning 1737) at 550°C, 40 Pa and with a silane (SiH_4) flow of 30 sccm. The deposition of a-Si by LPCVD eliminates the de-hydrogenation step needed before crystallization when using PECVD, due to the very low content in hydrogen. The metal layers (Al and Au) with different thickness (1, 2 and 5 nm) were deposited by e-beam evaporation. The samples were then annealed during 5, 10 and 30 h at 500°C. In order to evaluate the structural properties, spectroscopic ellipsometry (SE) using a Jobin-Yvon ellipsometer

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and X-ray diffraction (XRD) using a Rigaku difractometer were used. A BEMA (Bruggemann Effective Medium Approximation) [6] model was used to simulate the SE results. The crystallized Si was simulated using a two-layer model: one layer representing the bulk and the other the film's roughness. A mixture of poly-Si (simulates the crystallized fraction), a-Si (simulates the non-crystallized fraction) and voids (simulates the grain-boundaries and porosity) forms both layers [7]. Aluminium contacts were evaporated for dark conductivity measurements. Scanning Electron Microscopy (SEM) with a FE-SEM S-1400 Hitachi was used to analyse the film's morphology.

3. Results and discussion

3.1. Influence of metal thickness

The results of the BEMA model for samples prepared with different metal thickness (d_m) and annealed for 30 h are shown in Table I. The data indicate that the samples annealed using Au always present a higher crystalline fraction (f) independent of d_m. When using a metal layer with 2 nm the poly-Si sample crystallized with Au presents a fraction of 57.5% compared with 38.7% for Al. This difference becomes more pronounced as d_m increases. Further increase would not lead to any improvement in case of Al. On the other hand, in case of Au is visible a significant enhancement of f. The results suggest that the crystallization is more effective in presence of Au.

The dark conductivity (σ_d) results presented on Fig. 1 show the effect of d_m on the activation energy (E_A). An initial increase on E_A due the enhancement of f is observed. However with further increase on d_m this behaviour is inverted. It is possible to see that despite increasing the fraction (see BEMA data) a raise on the thickness leads to a decrease on the E_A of the poly-Si samples. This behaviour indicates an increase of the doping effect caused by metal incorporation. Another important fact is that this effect is even more pronounced in the Al case. Indeed an Al layer with only 2 nm is enough to induce a great doping effect.

Both metals form an eutectic with silicon but these results indicate that the crystallization kinetics is quite different. The MIC process occurs by diffusion and in the case of metals that do not form silicides by the formation of an intermixed layer. The Au-Si system has a eutectic temperature more than 200°C below when compared with the Al-Si system (363 and 577°C, respectively). This may lead to an important point that is the formation of a localized liquid phase on the samples with Au during the annealing since the MIC process was performed at 500°C. This liquid phase is formed where the Au contacts with the Si and may be responsible for an enhancement of the diffusion process since allows a better homogeneity of the mixture Au-Si [8]. The formed liquid reduces the activation barrier of the thermodynamically favourable a-Si to crystalline silicon (c-Si) transition. The mechanism proposed for this behaviour is based on a constitutional supercooling (CS), due to the lower melting point of the a-Si when compared with c-Si, which leads to a crystalline silicon precipitation [9]. The formation of a liquid phase at the interface is not supposed to occur in the Al-Si system

TABLE I Results of a BEMA model obtained by SE for samples annealed for 30 h with different d_m

			Au				Al			
Metal thickness	Annealing time		d (nm)	p-Si (%)	a-Si (%)	Voids (%)	d(nm)	p-Si (%)	a-Si (%)	Voids (%)
5 nm	30 h	Bulk	140.2	80.9	10.2	8.9	162.7	36.0	47.7	16.3
		Roughness	35.4	71.3	22.4	6.3	26.5	14.3		85.7
2 nm	30 h	Bulk	114.5	57.5	40.5	2.0	167.6	38.7	52.1	9.2
		Roughness	22.7	54.2	25.1	20.7	11.4	22.6		77.4
1 nm	30 h	Bulk	133.8	43.8	51.9	4.3	157.9	35.4	55.3	9.3
		Roughness	26.7	24.0		76.0	4.9	27.2		72.8

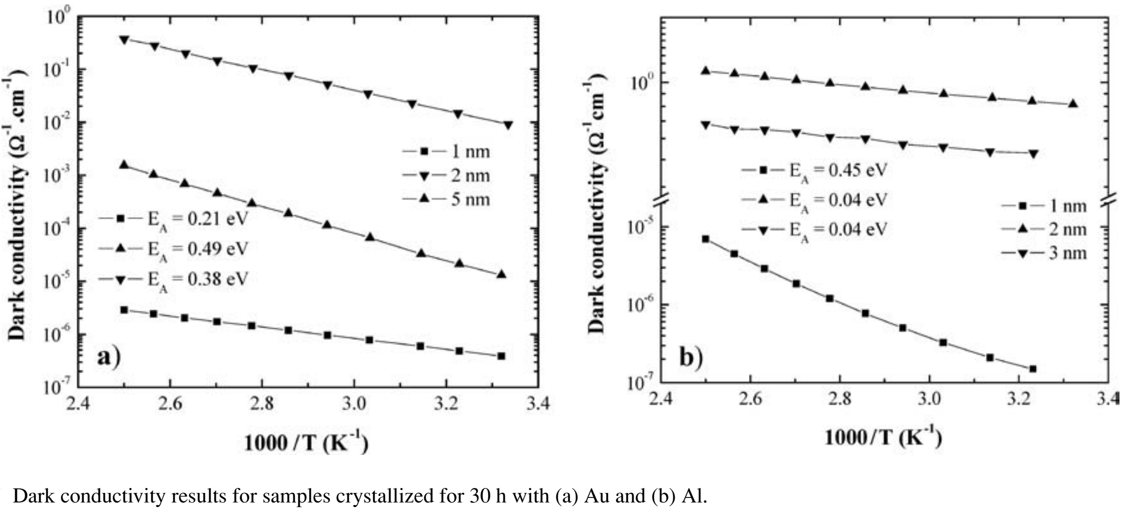

Figure 1 Dark conductivity results for samples crystallized for 30 h with (a) Au and (b) Al.

since the eutectic temperature is not reached and so all the reaction processes in solid state what reduces the effectiveness of the MIC process. In the initial stages of the reaction between the metal layer and the a-Si at temperatures below the eutectic temperature some metastable metal-Si compounds are formed. The formation of the nucleus of Si crystals must occur in this intermixed phase and then the migration of the Si to this phase and the Al to the Si will lead to the crystallization. For temperatures near the eutectic temperature the structure becomes more homogeneous and the metal segregates out from the formed poly-Si film [8].

The model for crystallization also suggests that after the process is complete, the metal will be segregated to the grains boundaries or to the bottom/top of the crystallized film. However as the crystallization is not so effective for the Al samples, they do not crystallize completely and so some metal remains in the intermixed phase and inside the a-Si. Besides leading to lower f, also leads to a great metal contamination and doping effect. Apart from that, the Au diffuses in silicon preferentially through interstitial sites [10] what may also lead to a lower effective doping by metal atoms in Au case since they will not occupy many substitutional electronic active sites.

The thickness of the metal layer will determine how deep will be the intermixed phase metal –Si. Since the crystallization is directly dependent on the formation of this intermixed phase, it will be enhanced with the increase on d_m. This behaviour is observed for both Au and Al. It is known that in Aluminium Induced Crystallization (AIC) process (a variant of MIC) the same thickness of Al and Si is used to get full crystallization for short periods of time [11].

The SEM images of samples prepared with 5 nm of metal are shown in Fig. 3. It is possible to see the difference in the morphology after annealing for 30 h. The Al (Fig. 3b) sample presents a smother surface, where some crystallites appear in a very smooth matrix that is supposed to be a-Si. When comparing the SEM images for samples prepared with Au and Al the larger f indicated by SE data for the Au samples is confirmed. For the Au the crystallization is almost complete and some of a-Si present in the BEMA model refers mainly to disorder zones at the grain boundaries and/or some un-crystallized zones at the bottom of the film. The morphology in Au sample (Fig. 3a) seems to be very homogeneous that may be due to the formation of the liquid phase.

3.2. Influence of the annealing time

As the MIC process is based in diffusion mechanisms, it is expected to be time dependent. In Table II it is shown the results for the BEMA model for samples annealed for different times with a d_m of 2 nm. As can

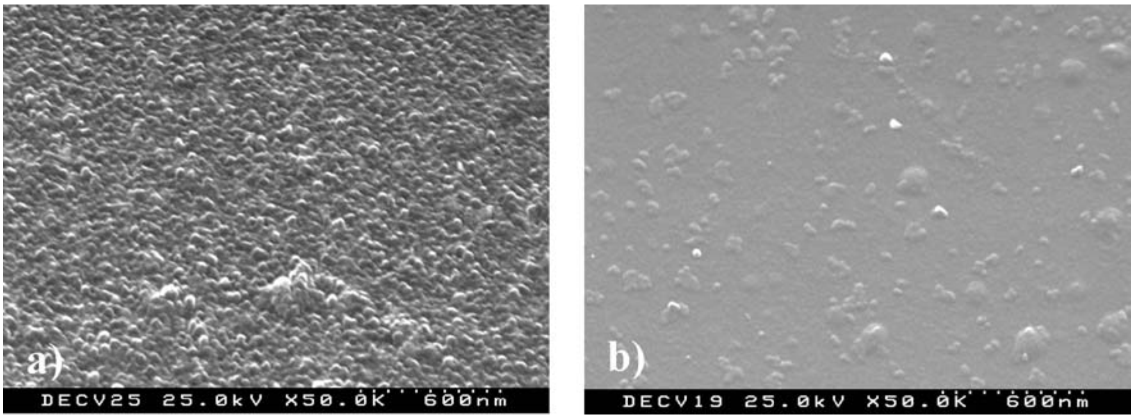

Figure 2 SEM images of samples annealed for 30 h with 5 nm of (a) Au and (b) Al.

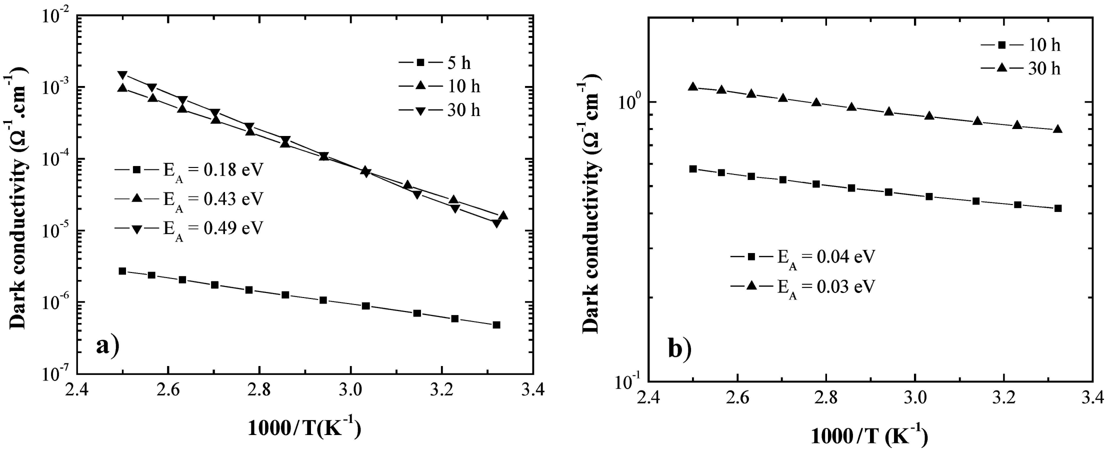

Figure 3 Dark conductivity results for samples crystallized with 2 nm of metal (a) Au and (b) Al.

TABLE II Results of a BEMA model obtained by SE for samples crystallized using 2 nm of metal for different t_a

			Au				Al			
Metal thickness	Annealing time		d (nm)	p-Si (%)	a-Si (%)	Voids (%)	d (nm)	p-Si (%)	a-Si(%)	Voids(%)
2 nm	5 h	Bulk	140.1	0	100	0				
		Roughness	12.2	0	39.1	60.9				
2 nm	10 h	Bulk	140.2	24.2	74.9	0.9	169.2	24.5	66.6	10.9
		Roughness	35.4	70.2	2.3	27.5	21.9	8.0		92.0
2 nm	30 h	Bulk	114.5	57.5	40.5	2.0	167.6	38.7	52.1	9.2
		Roughness	22.7	54.2	25.1	20.7	11.4	22.6		77.4

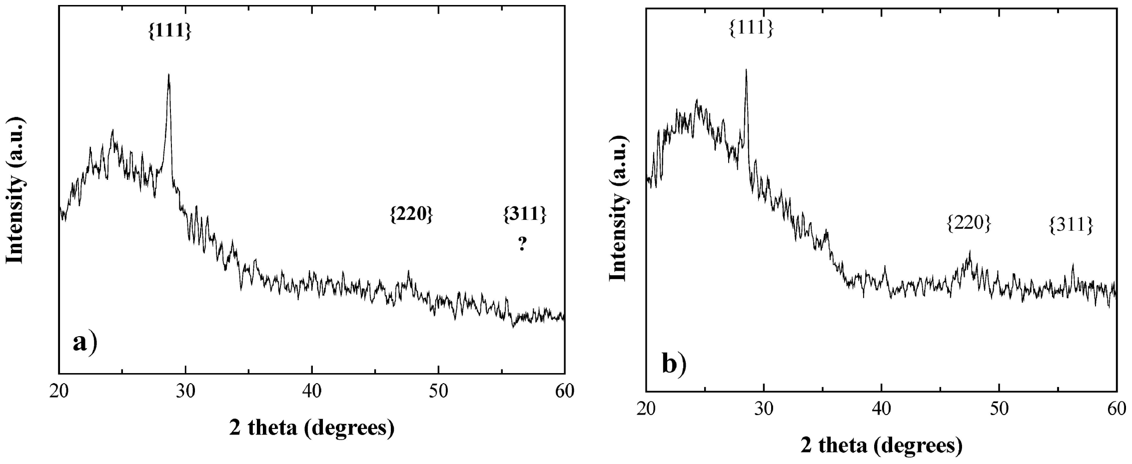

Figure 4 XRD patterns for samples annealed for 30 h with 2 nm of metal (a) Au and (b) Al.

be seen, the increase of the annealing time (t_a) leads to an enhancement on f. As stated before the diffusion at 500°C is much more effective in the Au-Si system due to the formation of a liquid phase and this is again confirmed by the SE data. The effect of t_a is much more pronounced in Au crystallized samples where it is observed an increase of f by more than two times when increasing t_a from 10 up to 30 h. The same does not happen in the sample with Al where the enhancement is not much more than 50%.

The effect on the σ_d is also observed in Fig. 3 where is notorious the increase of E_A as the annealing time rises. This is an indication of the increase on the crystallinity, since the values get closer to the mid gap value for c-Si (0.55 eV). However in case of Al the E_A almost do not increase, showing that despite the crystallization process occur, as shown by SE, the doping effect is very pronounced leading to low E_A. Another study shown than the doping effect in the Al crystallised samples can be reduced if the metal thickness remains around 1 nm. [12]. The difference on the doping effect was already explained above.

The formed poly-si films seem to be oriented in the same way independent on the metal used as shown by the XRD patterns (Fig. 4). They crystallize preferentially trough the {111} direction in both cases. Then the {220} direction is preferred and at last the {311} direction. No metal peaks are present indicating that it is completely dissolved on the silicon. Despite the differences on the crystallization process the {111} direction is preferred due to the lower surface formation energy [13].

4. Conclusions

Although presenting the same type of system (eutectic), Au and Au will react in different ways with Si depending on the annealing temperature. At 500°C the Au-Si eutectic temperature is exceeded and the formation of a liquid phase will enhance significantly the diffusion mechanism responsible for the MIC process. This will reduce the energy barrier for crystallization what leads to higher crystalline fraction when compared with samples crystallized at the same temperature using Al. The doping effect seems to be smaller in the Au case since as the crystallization advances the metal is segregated to the boundaries of the grains were become less active as dopant. Also the diffusion preferentially thought the Si interstitial sites of the Au atoms is responsible for the lower doping effect. In Al case the crystallization is not complete and the metal remains in Si and at the intermixed phase increasing the doping effect.

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References

1. S. Y. YOON, S. J. PARK, K. H. KIM and J. JANG, *Thin Solid Films* **383** (2001) 34.

2. S.-I. MURAMATSU, Y. MINAGAWA, F. OKA, T. SASAKI and Y. YAZAWA, *Sol. Energy Mater. Sol. Cells* **74** (2002) 275.
3. R. B. IVERSON and R. REIF, *J. Appl. Phys.* **62** (1987) 1675.
4. S. Y. YOON, K. H. KIM, C. O. KIM, J. Y. OH and J. JANG, *ibid.* **82** (1997) 5865.
5. S.-I. MURAMATSU, Y. MINAGAWA, F. OKA, T. SASAKI and Y. YAZAWA, *Sol. Energy Mater. Sol. Cells* 74 (2002) 275.
6. D. A. G. BRUGGEMANN, *Ann. Phys. (Leipzig)* **24** (1935) 636.
7. P. PETRIK, T. LOHNER, M. FRIED, L. P. BIRÓ, N. Q. KHANH, J. GYULAI, W. LEHNERT, C. SCHNEIDER and H. RYSSEL, *J. Appl. Phys.* **87** (2000) 1734.
8. L. HULTMAN, A. ROBERTSSON, H. T. G. HENTZELL, I. ENGSTRON and P. A. PSARAS, *ibid.* **62** (1987) 3647.
9. J. STOEMENOS, J. MCINTOSH, N. A. ECONOMOU, Y. K. BHATNAGAR, P. A. COXON, A. J. LOWE, and M. G. CLARK, *Appl. Phys. Lett.* **58** (1991) 1196.
10. L. CALCAGNO, S. U. CAMPINASO and S. COFFA, *J. Appl. Phys.* **66** (1989) 1874.
11. O. NAST, S. BREHME, S. PRITCHARD, A. G. ABERLE and S. R. WENHAM, *Sol. Energy Mater. Sol. Cells* **65** (2001) 382.
12. L. PEREIRA, H. AGUAS, R. M. S. MARTINS, P. VILARINHO, E. FORTUNATO and R. MARTINS, *Thin Solid Films* **451/452** (2004) 334.
13. R. J. JACCODINE, *J. Electrochem. Soc.* **110** (1963) 524.