Hydrogen Plasma-enhanced Crystallization of Amorphous Silicon for Low-temperature Polycrystalline Silicon TFT's

K. Pangal, J.C. Sturm and S. Wagner
Center for Photonic and Optoelectronic Materials, Department of Electrical Engineering
Princeton University, Princeton, NJ 08544 USA
Ph: 609-258-6624, Fax: 609-258-6279, email: kpangal@ee.princeton.edu

Abstract

It has recently been discovered that a room temperature hydrogen plasma could reduce the crystallization time at 600°C of hydrogenated amorphous silicon films by a factor of five to a reasonable four hours [1]. Further, the process can be spatially controlled by masking with a patterned oxide. In this abstract, we report for the first time the successful application of this method to an all low-temperature (≤ 600 °C) TFT fabrication process. Good performance with mobility of 40-35 cm^2/Vs and an ON/OFF ratio of $4x10^5$ has been achieved with a crystallization time of only four hours.

Introduction

The crystallization of amorphous silicon (a-Si) deposited by plasma enhanced chemical vapor deposition (PECVD) by thermal annealing is of great interest for display and silicon-on-insulator (SOI) technologies. Because of a larger grain size, such films typically have a much higher mobility than deposited polycrystalline films, but long anneal times (about 20 hrs) at 600 °C (upper limit for glass) make the process unattractive for manufacturing. Various techniques have been tried to decrease the crystallization time, such as metal-induced crystallization [2] and germanium-induced crystallization [3] and electron cylcotron resonance (ECR) oxygen-plasma-induced crystallization [4]. Of these methods, the plasma-induced crystallization potentially introduces the least contamination to the films. We have found that a room temperature RF hydrogen plasma treatment can significantly reduce the crystallization time beyond that achieved with an oxygen plasma treatment, and have used this technique to successfully fabricate TFTs with a greatly reduced crystallization time.

Hydrogen-plasma-induced Crystallization

The process begins with plasma-enhanced chemical vapor deposition (PECVD) of 150 nm of hydrogenated a-Si (a-Si:H) on 7059 glass at 150-350 °C (Fig. 1), followed by a room temperature plasma exposure in an RIE configuration to create seed nuclei, followed by crystallization of the film in N_2 at 600 °C. The change in reflectivity at 276 nm is used to monitor the degree of crystallization [4], with the saturation of the reflectance peak at 276 nm indicating complete crystallization (Fig. 2). Films which are not plasma-treated require 20 hrs to fully crystallize, while those subjected to an O_2 or H_2 plasma require only 8 or 4 hrs, respectively (Fig. 2). The typical grain size for plasma treated or untreated control samples as observed by TEM is ~0.5 μm. The grains of the completely crystallized polysilicon film are predominantly oriented in the (111) direction irrespective of prior treatment.

It has long been known that the exposure of a-Si:H to hydrogen radicals results in the abstraction of hydrogen from the surface, which results in the restructuring of the surface [5]. The impinging H atoms interact with the silicon-hydrogen surface unit to form volatile H_2 molecules. Hydrogen abstraction is thought to lead to the formation of micro-crystallites. In our work, during subsequent annealing, these crystallites grow leading to a polycrystalline film. Infrared absorption spectra of the plasma-treated a-Si:H films shows that hydrogen plasma treatment results in the formation of a shoulder at 2100 cm^{-1} corresponding to $Si\text{-}H_2$ bonds, characteristic of microcrystalline Si [6], in addition to the peak at 2000 cm^{-1} corresponding to Si-H bonds in a-Si:H, showing that the plasma treatment results in a micro-structural change at the surface [1]. Etching off the top 40 nm after plasma treatment before crystallization removes the beneficial effect of the plasma (Fig. 3). It also removes the characteristic 2100 cm^{-1} FTIR absorption peak induced by the plasma, which shows that the layer containing the micro-crystallites is about 40 nm. The clean nature of a H_2 plasma treatment avoids the residual metallic contamination effects from metal-overlayer-induced crystallization processes [2], in which metal segregates to the crystallization front.

SIMS analysis of the plasma-treated and untreated (control) a-Si:H films show that the plasma results in hydrogen abstraction from the surface (Fig. 4) [7]. The hydrogen plasma treatment had the most drastic effect with the surface hydrogen concentration falling from $3x10^{21}$ cm^{-3} to $1x10^{19}$ cm^{-3}, while the oxygen plasma treatment resulted in a hydrogen surface concentration of about $1.5x10^{20}$ cm^{-3}. These results are consistent with the fact that a hydrogen plasma treatment was more effective in reducing the crystallization time than an oxygen plasma treatment. SIMS (Fig. 5) also showed that the plasma treatment produced aluminum contamination, the source of which is the aluminum oxide electrode plate, which is being inadvertently sputtered onto the sample [7]. (The ~4 cm^2 samples were placed directly on an aluminum oxide coated electrode.) It is thought, however, that the concentration of

0-7803-4774-9/98/$10.00 © 1998 IEEE

aluminum (~10^{18}–10^{19} cm^{-3}) at the surface of the sample is insufficient to cause any significant change in crystallization times [8]. This was confirmed by placing the a-Si:H samples on a 100 mm silicon wafer during exposure to the plasma to reduce aluminum contamination to below 10^{17} cm^{-3}, which is the same as the untreated sample. These samples crystallized within the same time as the sample that was placed directly on the aluminum electrode.

TFT Fabrication and Results

I. LOW-TEMPERATURE TFTs (≤ 600 °C)

Thin film transistors (TFTs) were made in films not exposed to a plasma before crystallization (subsequent anneal time of 13-20 hrs), and films exposed to an oxygen (subsequent anneal time 7 hrs) or hydrogen (anneal time only 4 hrs) plasma before crystallization, with all crystallization done at 600°C. After crystallization, n-channel TFT's were fabricated by a standard self-aligned top-gate process (Fig. 4). After the films were completely crystallized, active area was defined by dry etching and a 150 nm gate oxide was deposited by PECVD at 250°C. The PECVD oxide was then annealed at 600°C in O_2 for 1 hr. A 300 nm a-Si:H layer doped in-situ with phosphorus (~10^{20} cm^{-3}) was deposited by PECVD at 240°C to form the gate. After the gate was patterned by dry etching, the P^+ source and drain ion implantation was done at 40 keV and a dose of $2x10^{15}$ cm^{-2}. The implant damage anneal and crystallization of the gate was done simultaneously by annealing at 600 °C in N_2 to limit the maximum process temperature to 600 °C. Finally aluminum contacts were evaporated and patterned. At the completion of processing a RF hydrogenation step was performed at 300°C, at a RF power of 0.6 W/cm^2 for 60 min.

Well-behaved characteristics were obtained in all cases (Fig's. 7,8). All samples had mobilities in the range of 35-45 cm^2/Vs despite the short crystallization time in the hydrogen-plasma treated sample (Table 1). The plasma treated samples show higher threshold voltages of ~3 V compared to 0.2 V for the sample without the plasma treatment. The higher threshold voltage is thought to be due to the aluminum from the aluminum oxide coated electrode being sputtered on to the sample during the plasma exposure as mentioned earlier (N_{Al} ~$5x10^{18}$ cm^{-3}) to dope the channel region p-type. The subthreshold slopes (1.3-1.6 vs. 2.6 V/dec) and the ON/OFF ratios (4-$7x10^5$ vs $2x10^5$) were both better in the plasma treated films with shorter crystallization times. The field-effect mobility increased slightly as the channel length was reduced (Fig. 10).

II. HIGH-TEMPERATURE TFTs (≤1000 °C)

N-channel self-aligned TFTs were also made using thermally grown gate oxide in films not exposed to a plasma before crystallization (subsequent anneal time of 20 hrs) and in films exposed to a hydrogen plasma (anneal time only 4 hrs) before crystallization. SiO_2 covered silicon substrates were used, instead of glass. The samples were exposed to hydrogen plasma by placing the samples on a large silicon wafer to eliminate the aluminum contamination. 35 nm dry oxide was grown at 1000 °C and annealed in N_2. The source and drain implant anneal was done at 850 °C in N_2. After the aluminum metal deposition and patterning, the samples were hydrogenated as in case of the low temperature TFTs.

The threshold voltage shift of the TFTs with the plasma treatment was much smaller in this case, consistent with the lower level of aluminum contamination. While the control and hydrogen plasma samples had similar mobilities within experimental error (Table 1), mobilities were again higher at short L (Fig. 10). The subthreshold slopes are also sharper than the low-temperature TFTs with values of ~ 0.6 V/decade (Fig. 9). Because the grain sizes for the films processed at high temperature is similar to that of the low-temperature films, the mobility and subthreshold slope difference may be due to the better Si/SiO_2 interface quality for the thermal oxides.

Summary

We have for the first time successfully fabricated low-temperature and high temperature TFT's with excellent characteristics using a hydrogen plasma-seeding treatment to greatly reduce the crystallization times of amorphous silicon films. The method is very attractive for high performance circuits on large-area glass substrates.

This work was supported by DARPA/ONR under contract no. 66001-97-1-8904 and Princeton Program in Plasma Science and Technology (DOE contract no. DE-AC02-76-CHO-3073).

References

[1] K. Pangal, J.C. Sturm and S. Wagner, to be published, Proc. Symp. Mat. Res. Soc. **507** (1998).
[2] H. Kim, J.G. Couillard and D.G. Ast, Appl. Phys. Lett, **72**, 803 (1998).
[3] D.K. Sadana, E. Myers, J. Liu, T. Finstad and G.A. Rozgonyi, Mat. Res. Soc. Symp. Proc., **23**, 303 (1984).
[4] A. Yin and S.J. Fonash, Tech. Dig. IEDM, 397 (1993).
[5] H. Shirai, D. Das, J. Hanna, and I. Shimizu, Appl. Phys. Lett., **59**, 1096 (1991).
[6] E. Srinivasan and G. N. Parsons, J. Appl. Phys., **81**, 2847 (1997).
[7] K. Pangal, J.C. Sturm and S. Wagner, submitted to Journal of Applied Physics.
[8] G. Radnoczi, A. Robertsson, H. T. G. Hentzell, S.F. Gong and M. A. Hasan, J. Appl., Phys., **69**, 6394 (1991).

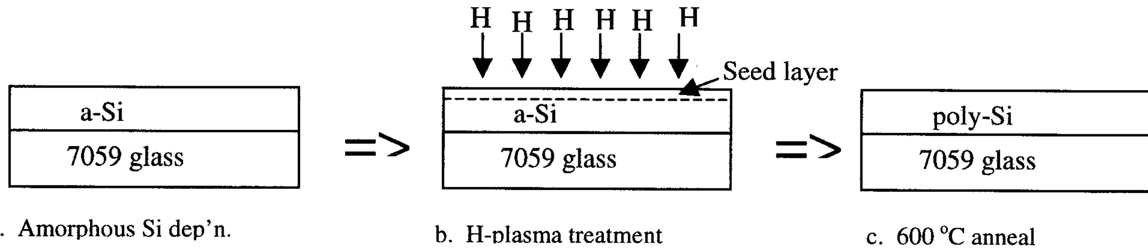

Fig. 1. Schematic diagram of the hydrogen plasma exposure process to reduce the crystallization time for low-temperature crystallization of amorphous silicon.

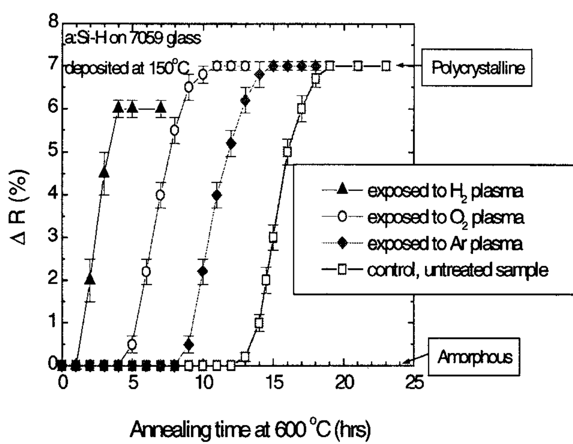

Fig. 2. Change in UV reflectance (276 nm) to measure crystallinity as a function of annealing time for samples exposed to different plasmas.

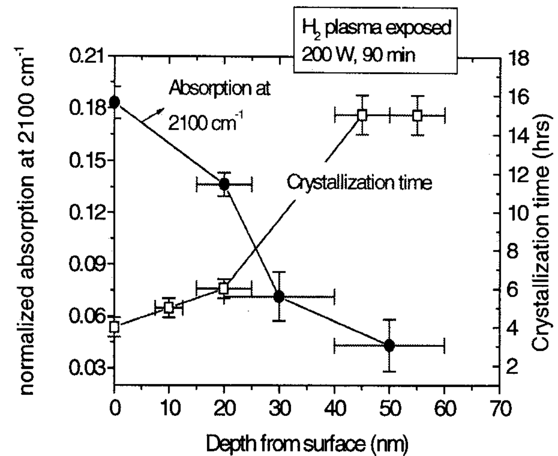

Fig. 3. Required crystallization time and 2100 cm^{-1} absorption as a function of etch depth after hydrogen plasma treatment showing that the direct effect of the plasma is confined to the top 40 nm.

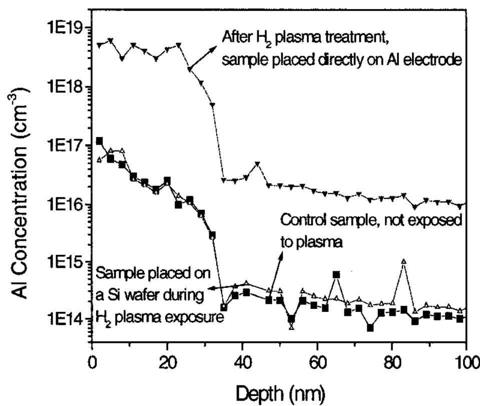

Fig. 4. Hydrogen concentration at the surface of the a-Si:H film before and after H_2 and O_2 plasma exposure, showing that hydrogen is depleted from the surface.

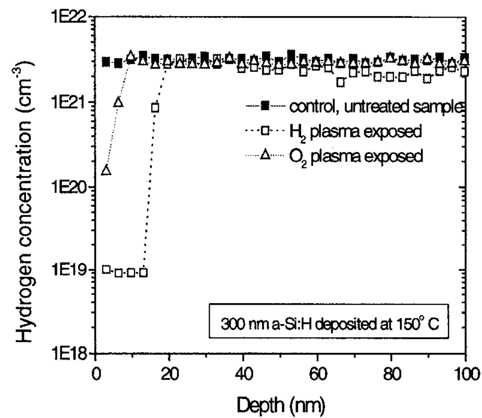

Fig. 5. Aluminum concentration at the surface of the a-Si:H films after H_2 plasma exposure with sample placed directly on the electrode vs. on a Si wafer.

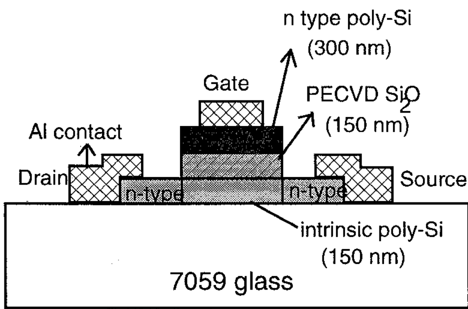

Fig. 6. Simplified low-temperature TFT cross section.

Table 1. Comparing the characteristics of both low and high temperature TFTs.

	Low Temperature TFTs (L=3.5 μm)			High Temperature TFTs (L=3.5 μm)	
	Control	O_2 plasma	H_2 plasma	Control	H_2 plasma
V_{TH} (V)	0.2	3.4	3.2	- 0.5	0.2
μ (cm^2/Vs)	45	40	35	105	96
S (V/dec)	2.6	1.4	1.6	0.6	0.57
N_{Al}(cm^{-3})	$<10^{17}$	-	$\sim 5x10^{18}$	$<10^{17}$	$<10^{17}$

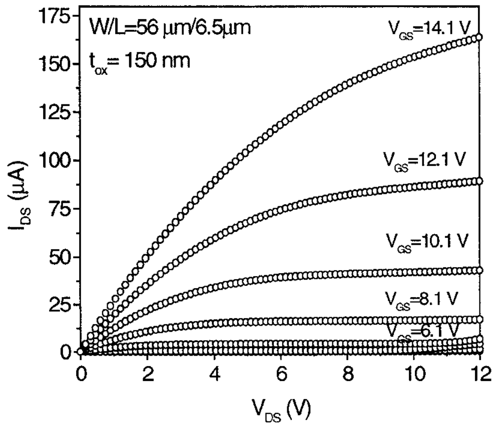

Fig. 7. Linear region characteristics of hydrogen plasma treated TFT's (W/L = 56 μm/13 μm).

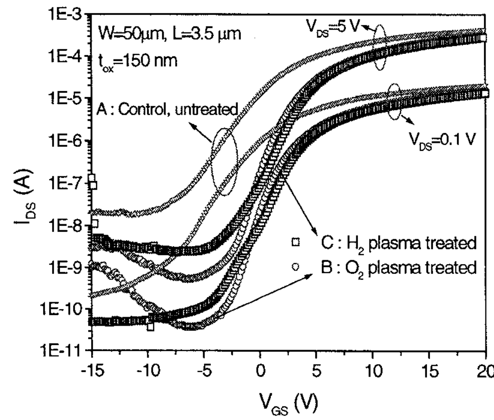

Fig. 8. Subthreshold characteristics of low-temperature poly-Si TFT's. Note 600 °C crystallization times of samples were different. (A: no plasma, 13-20 hrs; B: O_2 plasma, 7 hrs; C: H_2 plasma, 4 hrs).

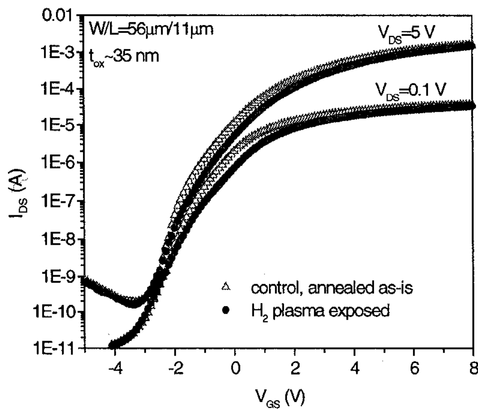

Fig 9. Subthreshold characteristics of high temperature poly-Si TFTs made of films annealed at 600°C with and without H_2 plasma treatment prior to anneal.

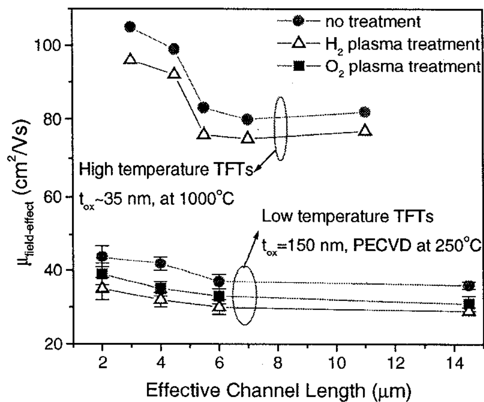

Fig. 10. Field-effect mobility of low-temperature and high-temperature TFTs for different channel lengths for untreated and plasma-treated films.