Thin Silicon Films on Polymeric Substrate

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Summary: Laser crystallization of amorphous silicon film on polymeric substrate is reported. Intrinsic amorphous films 1000 Å thick have been deposited on Polyethersulphone (PES) by PECVD technique in the deposition temperature range of 120-200 °C. Dehydrogenation and crystallization of the thin films have been obtained by high energy (10 J) XeCl pulsed excimer laser. The irradiation conditions have been varied to study their influence on dehydrogenated and crystallized material properties. Electrical and optical properties of as-deposited and crystallized films have been investigated. Structural characterization (SEM, XRD, AFM) has been performed. Average crystallite size and grain distribution have been evaluated.
For the substrate, the glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) have been evaluated by DSC (Differential Scanning Calorimetry) and TMA (Thermo Mechanical Analysis) measurements and the compatibility with the deposition and crystallization processes have been verified.

Keywords: DSC; polymeric substrate; pulsed laser crystallization; SEM; TMA; XRD

Introduction

There is a growing interest in replacing glass with plastic substrates to make large area electronic flexible devices. The primary advantages of plastic substrates are low costs, a reduction in the weight of the display, flexibility and reduction in display breakage, both during fabrication and use.

Silicon thin film technologies on polymeric substrates can be the key for the development of new cheap, portable, light-weight electronic appliances (new multimedia telephones, hand-held computer, digital cameras).

In the last years many efforts are attempting to reduce the maximum processing temperature for the electronic devices fabrication [1].

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High performance polymers are commercially available, featuring maximum processing temperature in the range of 200-250 °C, even higher for specialty and "niche" polymeric materials.

Amorphous silicon (a.Si-H) technology allows the deposition at low temperature of semiconductor films on polymeric substrates [2]. These films can be crystallized by means of pulsed excimer laser irradiation, the only method capable of producing polycrystalline silicon on polymeric substrates. Thermal budget of the whole process is consistent with the safeguard of the polymeric substrate. In fact a high energy but short laser pulse is used and inorganic buffer layer can be deposited between semiconductor layer and polymeric substrate to prevent contamination and crystallization thermal wave impinging on substrate [2]. The development of this process allows to conjugate the use of plastic substrates with the temperatures imposed by silicon crystallization kinetics.

The aim of this work is to describe an a-Si-H deposition process compatible with polymeric substrate and to determine optimised parameters of excimer laser crystallization.

Electrical, optical and structural properties of crystallized films are reported and correlated with crystallization process parameters.

The glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) of the PES substrate have been guide line to access better deposition and crystallization experimental conditions to avoid any substrate deformation or silicon film pill up and stress.

Experimental

A preliminary step in the present work has been performed to define the highest limit for processing temperature: the substrate glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) have been evaluated by DSC (Differential Scanning Calorimetry), DMA (Differential Mechanical Analysis) and TMA (Thermo Mechanical Analysis) measurements and the results are shown in table 1.

A 800 nm thick SiO_2 layer has been deposited on the polymeric substrate by Plasma Enhanced-Chemical Vapour Deposition (PECVD) (see table 2), at a pressure of 600 mTorr and with a RF power of 5 W. This layer has the role of a thermal barrier to protect the plastic substrate during laser processing and has the function to provide a smooth surface for deposition of the subsequent layer.

Amorphous thin silicon films (100 nm thick) have been deposited by PECVD on SiO_2 layer. The process gas is pure SiH_4 at a pressure of 750 mTorr and with a RF power of 3 W. The film growth rate is approximately of 1.4 Å/sec. The deposition conditions are shown in table 2.

The crystallization process has been performed by a new high energy excimer laser (Xe-Cl at 308 nm) "Hercules-L", a prototype laser completely designed by ENEA researchers, with a maximum energy output of 10 Joule, a pulse width of 120 ns, a maximum repetition rate of 10 Hz. The beam spot size is 100 mm x 70 mm. The samples, irradiated in air at room temperature, have been placed on a computer controlled x table, with position accuracy of 1μm, to obtain a uniform irradiation along the whole surface.

The laser beam has been focused on the sample by homogenisation optics to obtain a flat-top beam profile of 100 mm x 13 mm. The homogenisation system allows the continuous energy density control in the range between 120 and 1200 mJ/cm^2. This fine control of the processing parameters ensures the required flexibility for the a-Si crystallization without any damage of polymeric substrates.

In order to prevent severe damage of the a-Si:H films, resulting from crystallization process and due to the high hydrogen content in the films, a preliminary dehydrogenation is performed by irradiating the film at an energy density (fluence) in the 120-160 mJ/cm^2 range.

The pulse energy density necessary to film crystallization has been varied from 190 mJ/cm^2 to 220 mJ/cm^2.

Amorphous and crystallized samples have been characterized by a Perkin Elmer λ-900 UV/VIS/NIR spectrophotometer in the 250-500 nm wavelength range with reflectance measurements.

Electrical characterizations have been performed with coplanar silver paste contacts on the crystallized thin films by HP4140 pA meter/DC voltage source to evaluate film resistivity.

The film crystalline structure has been investigated by XRD measurements carried out with an X'PERT-MPD (Philips) diffractometer using a Cu K_α radiation source. X-ray diffraction analysis was performed in the range of 2Θ values from 20° to 60° with step of 0.05° and a time of measurement per step of 45 seconds. Crystallite size has been evaluated from XRD spectra performed in classical Bragg-Brentano configuration. XRD measurements in thin film configuration, with a incident grazing angle of 0.7°, are carried out to enhance the film signal

with respect to the substrate.

Film morphology and average grain size have been determined by Scanning Electron Microscopy (SEM) analysis.

The morphological analysis is completed with Atomic Force Microscopy (AFM) measurements by Digital Instruments Nanoscope IV and the film roughness is evaluated.

Results and Discussion

The DSC thermal analysis technique measures heat flows and phase changes on a sample under thermal cycles. A constant thermal rate of 10°C/min. in N2 fluxage has been kept for DSC measurements. The temperature associated with endothermic transition measured by DSC analysis technique on the amorphous thermoplastic polymer PES gives clear evidence of its glass transition Tg. Figure 1 shows the DSC measurement results.

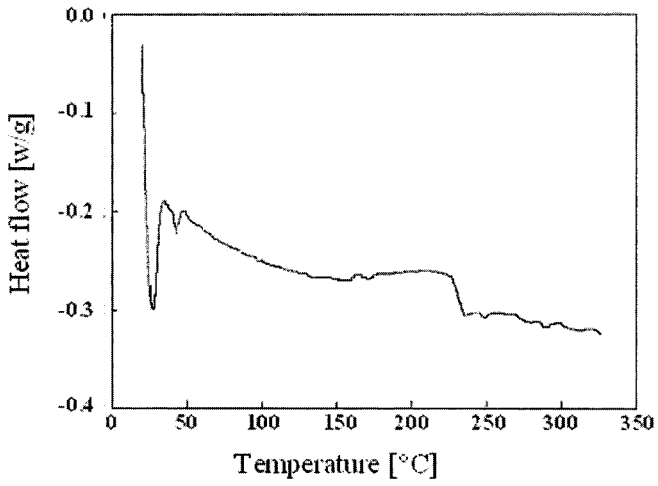

Figure 1. DSC measurement of PES.

The TMA measurements give dimensional changes in length, width, and thickness and allow to determine the coefficient of linear expansion (CTE) of the materials as a function of temperature or time under a controlled atmosphere. Figure 2 shows the TMA measurement results.

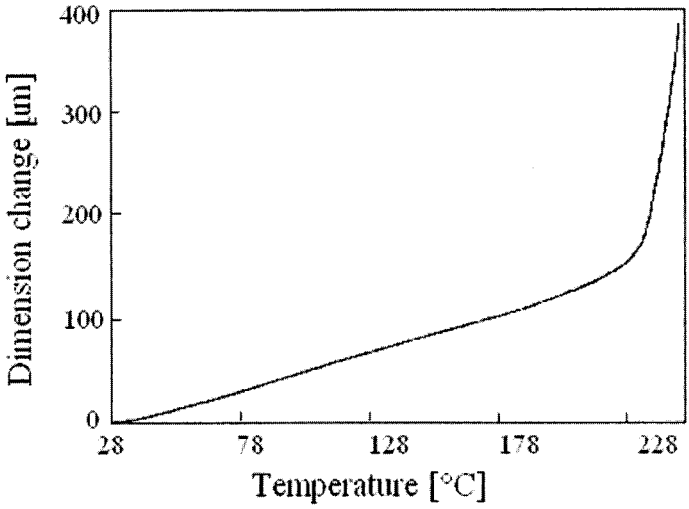

Figure 2. TMA measurement of PES.

Table 1. Glass transition temperature (T_g) and coefficient of thermal expansion (CTE) of PES.

Substrate	Tg [°C]	CTE [µm/m°C]
PES	220	57

Table 2. PECVD deposition conditions.

Substrate	Pressure [torr]		Power [W]		PECVD Dep. Temperature [°C]
	SiO_x	**a-Si:H**	**SiO_x**	**a-Si:H**	
PES	0.6	0.75	5	3	150

In figure 3 and 4 SEM images of crystallized films on PES substrate, irradiated with different laser fluences, 170 mJ/cm^2 and 220 mJ/cm^2 are shown respectively.

The grain size increases from 50 nm to 100 nm by increasing the irradiating fluences.

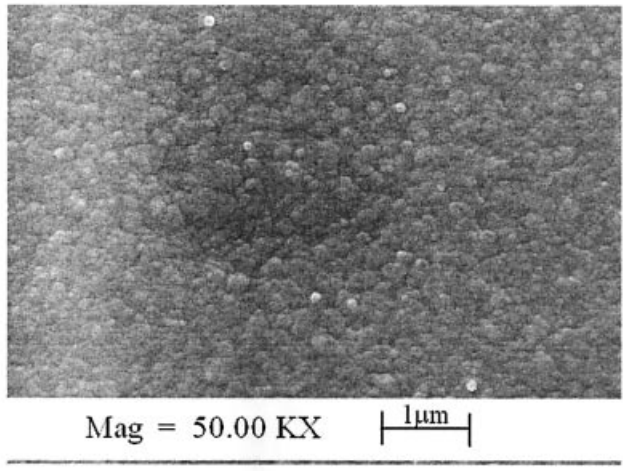

Figure 3. SEM images of film crystallized on PES with one laser pulse at fluence of 190 mJ/cm^2.

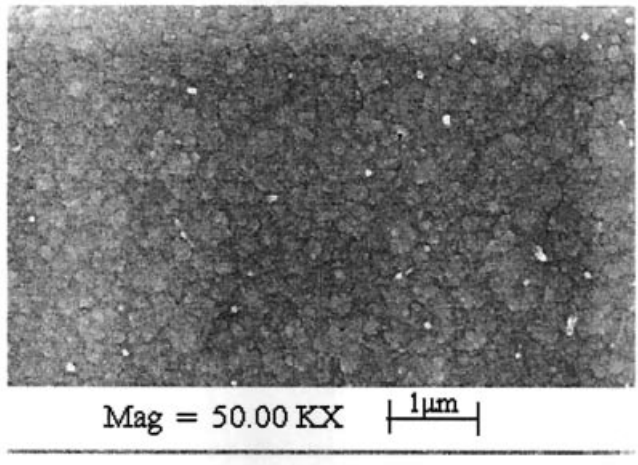

Figure 4. SEM images of film crystallized on PES with one laser pulse at fluence of 220 mJ/cm^2.

Reflectance spectra of amorphous and crystallized thin film on PES substrate are shown in figure 5: the prominent maxima at 273nm and 365nm are due to direct optical transition in the

k-space [4,5] typical of a crystalline phase. The reflectance spectrum of the amorphous film does not present these peaks. The prominence of these maxima is more evident increasing the radiation fluence.

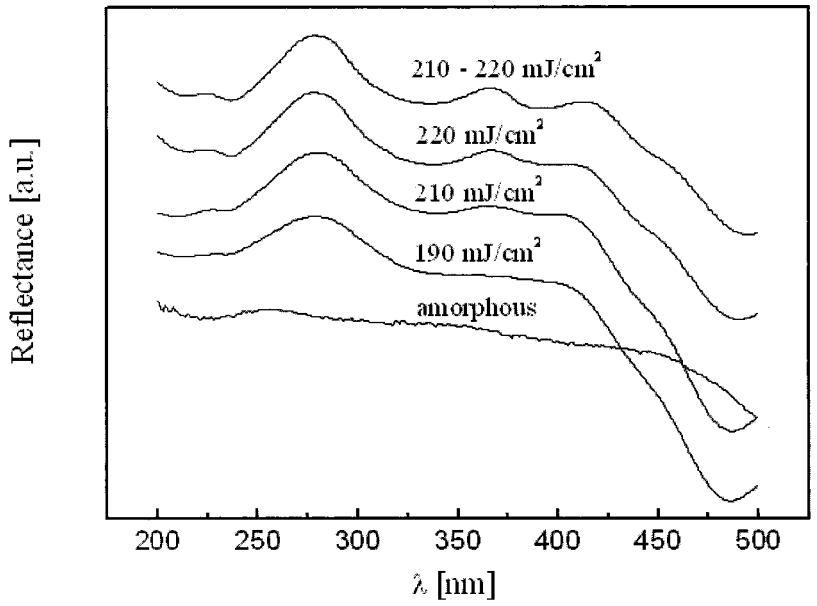

Figure 5. Reflectance spectra of amorphous and crystallized thin film on PES substrate.

XRD analysis confirms the crystallization process by excimer laser for each of irradiation fluence.

The crystallite sizes were calculated by Debey-Sherrer formula from the width at half maximum intensity (FWHM) of the peaks from XRD spectra obtained in Bragg-Brentano configuration. The crystallite size increases increasing the irradiation fluence. Crystallized films on PES substrate were investigated by XRD measurements in thin film configuration too. The spectra with different irradiation fluences in the 190-220mJ/cm^2 range are shown in figure 6. The measurements give evidence of the films crystallization and confirm the increased crystallite size on increasing laser fluence.

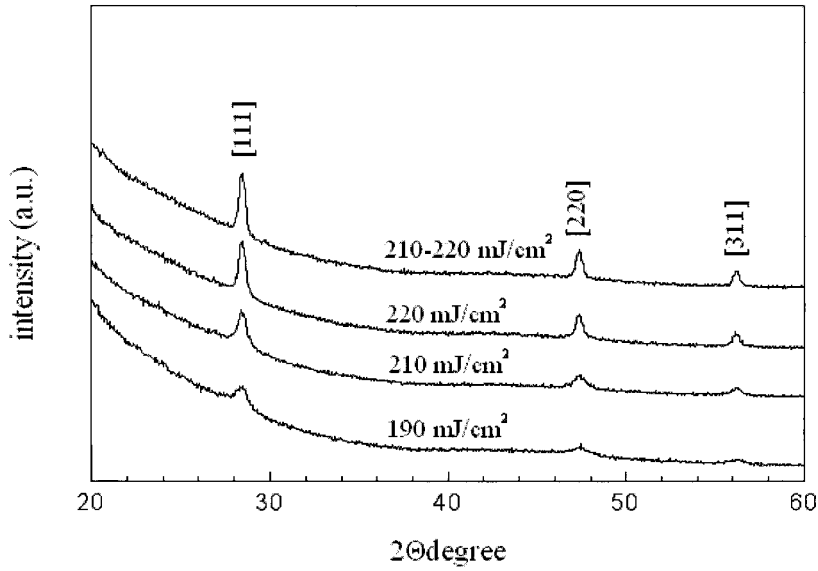

Figure 6. XRD spectra of crystallized film on PES varying the irradiation fluences in the 190 220mJ/cm^2 range.

The average crystallite sizes are reported in figure 7 as function of the irradiation energy density: the crystallite size increases from 180Å up to 550Å for the maximum fluence.

The two points at 220mJ/cm^2, the maximum irradiation fluence utilized, are obtained with different crystallization procedure. The point at lower crystallite size (550Å) is obtained with a single shot, while the other one (750Å) is obtained with two shots at 210 and 220 mJ/cm^2.

For the same samples, the electrical resistivity versus the fluence values is plotted in figure 7, too. The basic correlations between laser irradiation condition and electrical conductivity may be enhanced. The electrical resistivity decreases with increasing laser fluences and crystallite sizes. Supposing, for these films, a density carrier equal to the intrinsic crystalline silicon one [6], the mobility values are in the range 50÷190(cm^2/V s) increasing with the crystallite sizes. It can be supposed that the electrical transport is limited by the crystallite sizes.

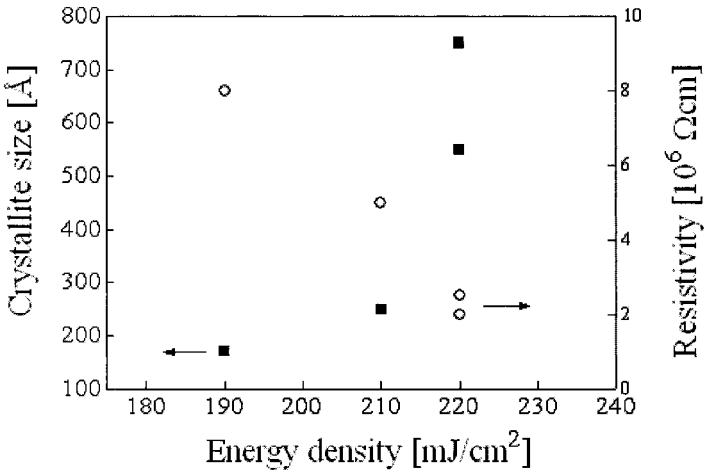

Figure 7. Average crystallite sizes and film resistivity as function of the irradiation energy density for thin film on PES substrate.

Figure 8 shows the average surface roughness of the excimer laser annealed Si films on PES substrate versus irradiating fluences. The average roughness values obtained from AFM images are in the range 4-10 nm.

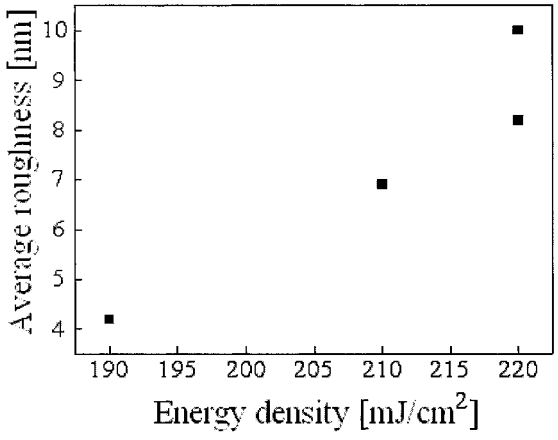

Figure 8. Average surface roughness obtained from AFM images of thin film on PES substrate.

Conclusions

Hydrogenated amorphous silicon films on PES substrates have been irradiated in air by a pulsed XeCl excimer laser to dehydrogenate and then to crystallize the films. Using carefully controlled conditions uniformly crystallized area was obtained. Increasing the radiation fluences the average crystallite size increases.

Furthermore, keeping the maximum fluence, the crystallite sizes increase carrying out radiation with intermediate fluences.

After crystallization the electrical resistivity of the films degreases with increasing the radiation fluences and therefore increasing the crystallite sizes.

Acknowledgement

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