*Sciences* & Technologie **A** – **N°26**, Décembre. (2007), pp. 27-32

# CRYSTALLIZATION OF THIN AMORPHOUS SILICON LAYERS BY VARIOUS LASERS

*Reçu le 08/04/2007 – Accepté le 05/09/2007*

**N. BOUKHEIT** [1]
**K. MIROUH**[2]
**A. KARAALI**[1]
1. Laboratoire des Propriétés Thermodynamiques et traitements de Surface des Matériaux
2. Laboratoire des Couches Minces et Interfaces, Département de Physique,
.Université Mentouri-Constantine
Algérie

## Résumé

Les lasers rubis pulsé, YAG pulsé et balayé et $CO_2$ continu ont été utilisés pour cristalliser des couches minces de silicium amorphe non dopé déposées par C.V.D. sur deux types de substrats : silicium monocristallin d'orientation (100) et la silice fondue amorphe ($SiO_2$).
Les couches recuites ont été caractérisées par microscopie électronique à transmission (MET) (coupes planes et transversales) et rétrodiffusion RUTHERFORD des ions d'hélium (RBS). Les effets de la nature du substrat et la quantité importante de l'azote présent dans les couches déposées sont étudiés. Les observations effectuées dans cette étude sont discutées qualitativement.

***Mots clés:*** Silicium amorphe, films minces, lasers Rubis-YAG-$CO_2$, MET, RBS, Cristallisation

## Abstract

Pulsed ruby, pulsed and scanned YAG, and $CO_2$ lasers have been used to crystallize thin C.V.D. deposited amorphous undoped silicon layers. Substrates are singlr crystal Si (100) or amorphous $SiO_2$.
The annealed layers have been investigated by RBS and TEM, using both plan viewed and cross - sectional samples. The roles played by the nature of the substrate and by the large amount of nitrogen in the deposited layers are studied. The major observations made during these investigations are qualitatively discussed.

***Keywords:*** *Amorphos silicon, Thin films, Ruby*- YAG-$CO_2$, TEM, RBS, Cristallisation

## ملخص

في هذه الدراسة تم استعمال ثلاثة أنواع من الليزر،الأول هو ليزر نبضي من نوع RUBIS و الثاني هو ليزر نبضي و ماسح من نوع YAG و الأخيرهو ليزر غازي من نوع ثاني اكسيد الكربون $CO_2$ المستمر لأجل بلورة شرائح رقيقة من السيليكون اللامتبلور و غير مطعم تم تحقيقها بتقنية تبخر الكيميائي (CVD). المساند المستعملة هي عبارة عن سيليكون (Si) احادي البلورة بالإتجاه (100) أو مادة ثاني أكسيد السيليكون ($SiO_2$ اللامتبلور). تم فحص الطبقات المعالجة (الملدنة) بواسطة تقنيتين هما : مطيافية روذورفرد (RBS) و المجهر الإلكتروني النفاذ (TEM) و ذلك على جهتين للعينة، الجهة المستوية و الجهة المقطعية. إن الأدوار التي تلعبها طبيعة المسند و الكمية الكبيرة لمادة النتروجين في الشرائح تمت دراستها. و أخيرا قمنا بمناقشة الملاحضات الهامة في هذه الدراسة بصورة كيفية.

**الكلمات المفتاحيـــة** : سيليكون اللامتبلور ، الصفائح الرقيقة ، الليزر ، المجهر الألكتروني النفاد ، مطيافية رودرفرد ، التبلور.

## Introduction:

Extensive researches have been performed on the surface processing by laser beams (1-6). This technique, which was first used to remove displacement damages in ion implanted silicon (7,8) broadened to encompass other fields and other materials. Among new applications of laser processing of materials, crystallization of amorphous layers of semi-conductors is of great interest.

During the last two decades and more, the laser crystallization of thin amorphous silicon layers has been studied extensively (9-12). Furnace annealing usually requires long anneal times, and induces the heating of both Si layer and substrate. However, in the case of the laser annealing, all of the laser energy is deposited directly into the silicon film in very short time (13). Consequently, laser crystallization appears to be more promising and has become one of the leading techniques for the fabrication of mono or polycrystalline silicon. Different types of laser and several modes of irradiation (pulsed, scanned) have already been used to crystallize the amorphous silicon films.

This paper deals with some particular aspect of the recrystallization process. Pulsed ruby, pulsed and scanned YAG and CW $CO_2$ lasers have been used to anneal thin layers of amorphous silicon deposited on both single crystalline Si (100) and fused silica substrates. Systematic investigations of the crystallized layers have been performed by mean of transmission electron microscopy (TEM) and Rutherford Backscattering (RBS) of helium ions

## II. Experimental:

Thin layers (1000 and 2000 Å) of amorphous undoped silicon, have been deposited by chemical vapor deposition (CVD) at 645 °C under nitrogen flux on two types of substrates: (100) oriented silicon crystal wafer and fused silica.

The amorphous layers have been crystallized by mean of various lasers: pulsed ruby, pulsed and scanned YAG and continuous $CO_2$.

Cross-sectional specimens were prepared using face to face gluing, mechanical thinning, dimpling and milling with an $Ar^+$ ion beam. Top-view samples were performed by dissolution the quartz substrate in HF acid. Transmission electron microscopy investigations were carried out using a PHILIPS EM300 electron microscope operating at 100 kV.

In the case of the RBS analysis, the samples are bombarded with 2 MeV helium ions from a Van de Graaff electrostatic accelerator and the scattered particles are detected by surface barrier detector.

Cross section of the as-deposited amorphous silicon is shown in figure 1. This layer has also been characterized by aligned and random RBS (fig.1).

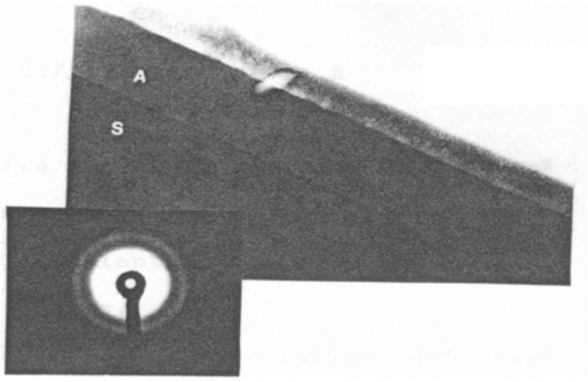

Fig.1 : Cross-section of amorphous Si layer deposited on Si(100) substrate S : substrate A ; amorphous silicon T : glue

## III. Results and discussion:

### III. 1. Pulsed Ruby Laser:

A 2000 Å thick amorphous Si on a Si (100) substrate has been annealed with a 20 ns pulsed ruby laser. Energy density was 1,5 J/cm$^2$ and the diameter of spot was approximately 8 mm.

Aligned and random spectra realized, with 2 MeV $He^+$ ions, for one and three shots exhibit the bad crystallinity of the laser annealed layer (fig.2). It can be deduced that the back interface moves towards the surface as a function of the number of shots.

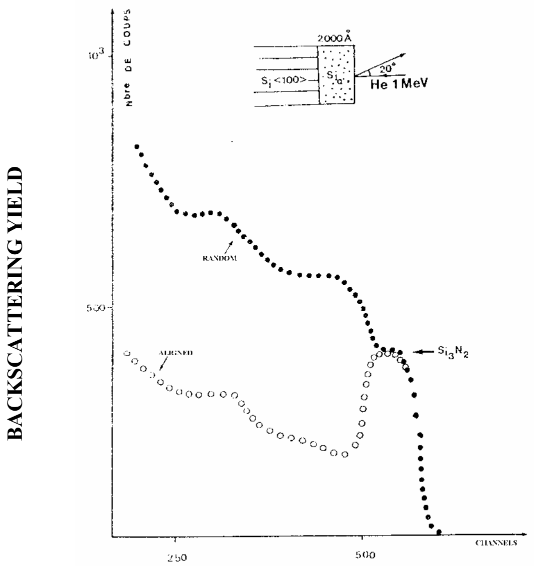

Fig.2 : RBS spectra showing the amorphous layer

Even after three shots a large residual disorder still exists. These results are readily explained by the occurrence of quasi-liquid phase in the irradiated layer. Transition with the single crystal occurs when the melted layer wets the underlying single crystalline substrate (14). After three shots the thickness of the disordered region is approximately 1000 Å. At the TEM scale, systematic observations exploring the surface of the laser spot show a strongly disordered layer (fig.3), thickness of this layer is around 1000 Å in good agreement with the result obtained from RBS spectra. This layer intricate internal substructure and is mainly polycrystalline as indicated by the spotty rings of the diffraction pattern. Through examination of this pattern shows some extra spots which do not belong to the diamond structure of silicon.

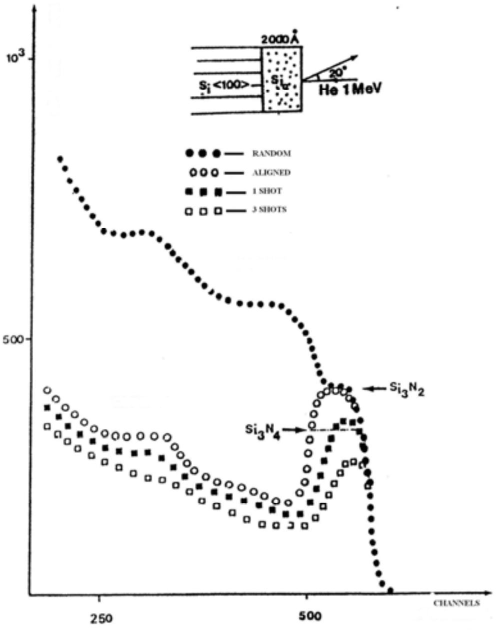

Fig.3 : RBS spectra of the layer irradiated by 1 and 3 shots of Ruby laser (20ns, 1,5 J/cm$^2$)

Calculation of the corresponding interplanar distances leads to the structure of the silicon nitride: $Si_3N_4$.
Silicon nitride has rather the shape of precipitates inside a disordered polycrystalline layer of silicon. These precipitates are likely responsible for the failure of a complete recrystallization of the amorphous silicon layer.

### III.2. Pulsed and Scanned YAG Laser:

Pulsed and scanned YAG laser (100 ns, 1,5 and 2,5 J/cm$^2$) has been used to anneal a 1000 Å thick amorphous Si layer on Si (100) substrate and 1300 Å thick layer on amorphous $SiO_2$ substrate. The amorphous layers contain a large amount of nitrogen which obviously modify the optical and thermal transport properties of the material. Therefore it is difficult to predict, from theoretical model (10), what is the energy density threshold which leads to the single crystal transition, when the melted front will wet the back interface with monocrystalline substrate (fig.4 and 5).

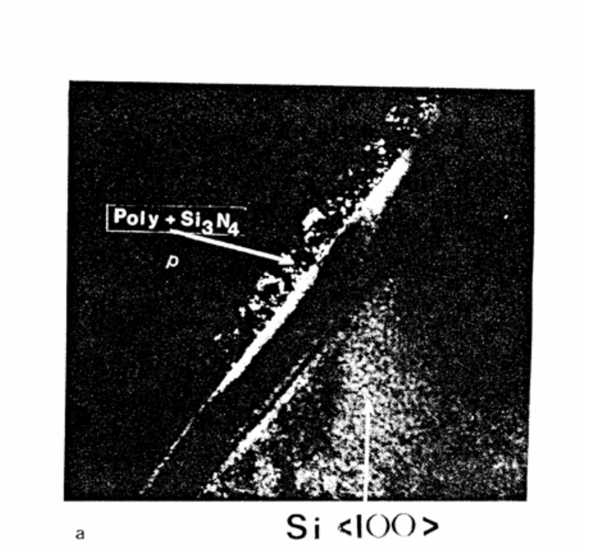

Fig.4 : a)Cross-section of the 2000 Å amorphous Si layer irradiated by 3 shots of Ruby laser (20ns, 1,5 J/cm$^2$)
b) associated diffraction pattern

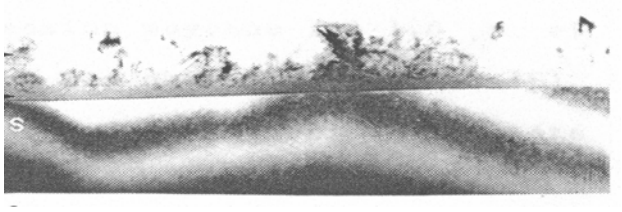

Fig5 : Cross-section of the 1000 Å amorphous Si layer irradiated by 3 shots of YAG laser (1,5 J/cm$^2$)

For 1,5 J/cm$^2$, a thin amorphous layer (200 Å) is still present between an outermost layer of polycrystalline material and the monocrystalline substrate. Obviously the energy density was not enough to promote recrystallization (fig.4).
Energy density of 2 J/cm$^2$ seems to be the threshold for a complete recrystallization (fig.5).
Systematic investigation exhibit intermixed poly and monocrystalline areas with a high density of twins. Extra spots in the diffraction pattern show evidence of presence of $Si_3N_4$.
When the substrate is amorphous $SiO_2$ the results appear quite different. With an energy density of 2 J/cm$^2$ for several scans, very large grains (1,5 µm) almost free of crystalline defects are observed (fig.6).

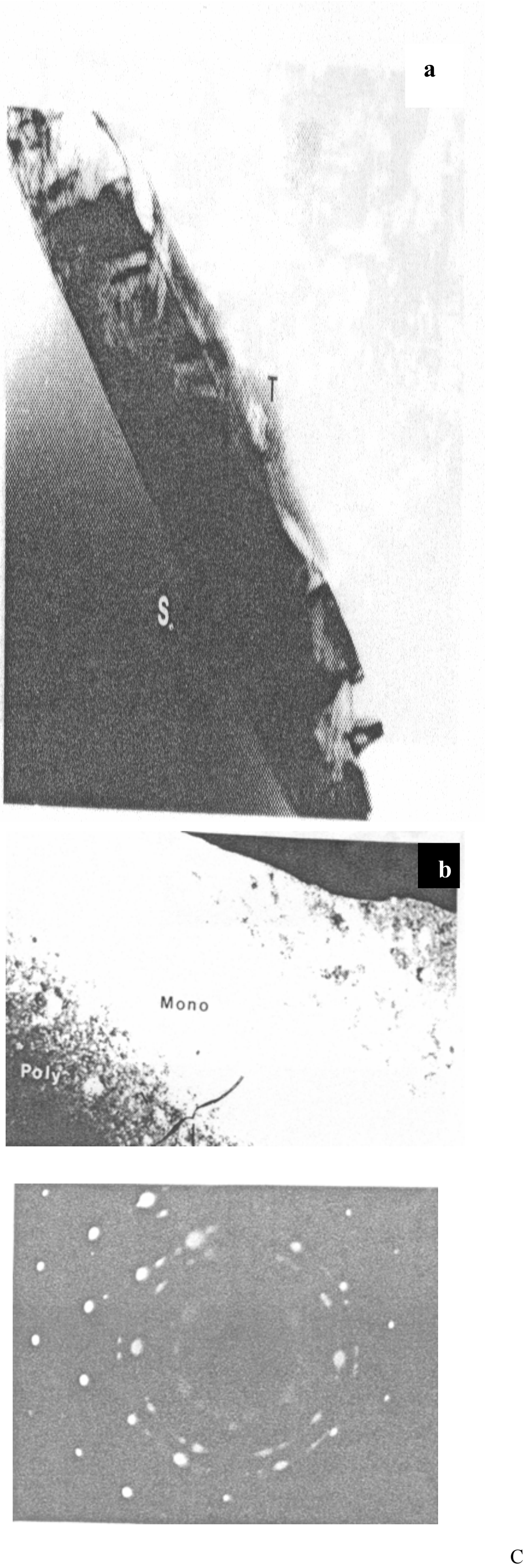

Fig.6 : a) Cross-section of the 1000 Å amorphous Si layer irradiated by 3 shots of YAG laser (2 J/cm$^2$)
b) alternated poly and monocrystalline regions
c) associated diffraction pattern

The preferential crystallographic orientations have not been noticed among the grains. The difference with above results comes from the different nature of the substrate which is, in this case later case, an efficient heat barrier.

For the first passage of the laser pulsation, the vertical heat is more important, i.e. that the speed of solidification, related to the optical absorption coefficient of material, is very important (a few m/s). The grains growth finishes on the surface of the sample. Their average size is equal to the thickness of the initially amorphous layer. With the second laser scan, an already crystallized part is subjected to this novel pulsation. This involves a competing influence of lateral and vertical heat flow, caused by the decrease of the optical absorption coefficient of material, and consequently the diminution of the solidification rate. The temperature gradients, in the sense of the scan of the laser beam, force the propagation of the crystallization front along the surface sample. Thus induces the formation of very large silicon grains.

### III.3. C. W. CO$_2$ laser:

C. W. CO$_2$ laser has been used to anneal a 1800 Å a thick amorphous Si layer deposited on an amorphous fused silica substrate.

Depending on the energy and on the number of scans, liquid phase, solid phase and explosive crystallization can take place. Here we report only the more interesting result, which is obtained with energy of 15 W for several scans. TEM observations show evidence of very large grains of silicon (10 µm) of a good internal quality in the middle part of irradiated ribbon (fig.7). Away from this ribbon, the heat decreases and polycrystalline structures are observed.

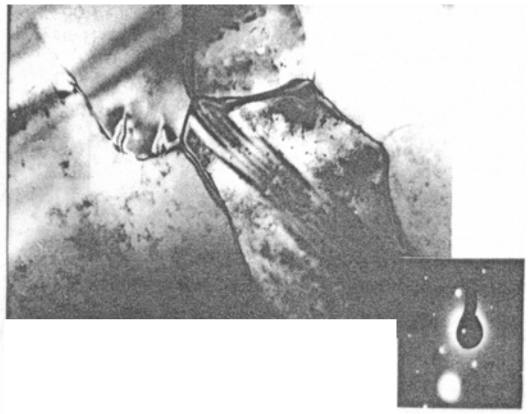

Fig.7 : Plan view of the amorphous silicon layer deposited on fused silica substrate and irradiated by the pulsed and scanned YAG laser (2 J/cm$^2$)

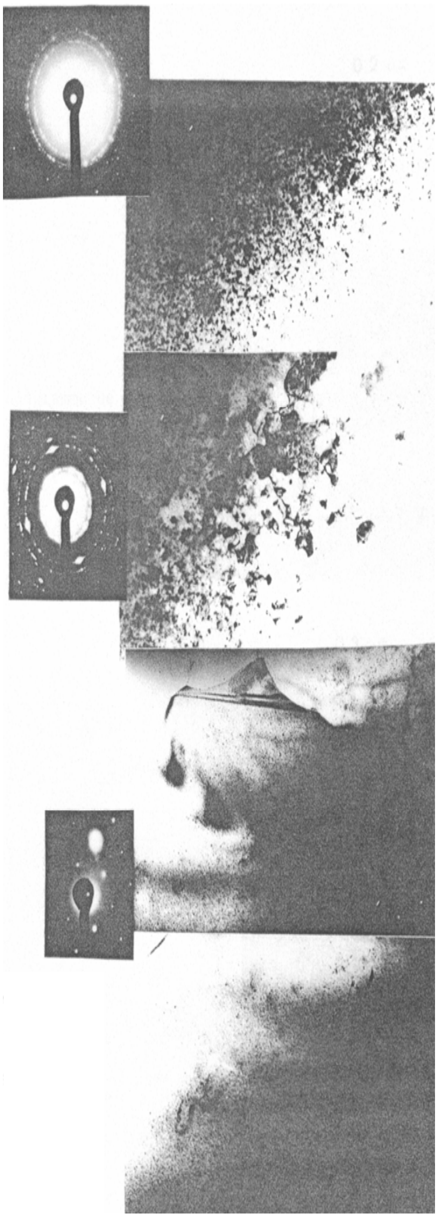

Fig.8 : Plan view of 1800 Å thick amorphous Si layer deposited on fused silica substrate and irradiated by the C.W. $CO_2$ laser.

## CONCLUSION

Laser processing of thin amorphous silicon layers gives rather intricate results. In most of the cases described above. Nitrogen, inside the deposited layers, interferes with the transient surface melting and can leads to the formation of silicon nitride precipitates, which prevent any further good crystallization.

Rather good and promising results are obtained with scanned laser and SOI structure. Very large grains of silicon are obtained.

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