PROCEEDINGS OF INTERNATIONAL CONFERENCE
NANOMEETING - 2013

PHYSICS, CHEMISTRY AND
APPLICATIONS OF NANOSTRUCTURES
REVIEWS AND SHORT NOTES

Minsk, Belarus, 28 - 31 May 2013

editors

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AFM and FTIR spectroscopy were applied to study the relationship between surface blisters and nanovoids in annealed hydrogenated a-Si. The influence of the H bonding configuration on the way the nanovoids give rise to the blisters is discussed. Annealing causes an increase of the polymers density. As they reside on the voids walls their density increase causes an increase of the voids volume. The polymers may release H inside the voids with creation of H₂ gas, whose expansion, upon annealing, further contributes to the volume increase of the voids till the formation of surface blisters.

1. Introduction

Nanovoids are still one of the major defects in hydrogenated amorphous Si (a-Si) [1]. Like in other amorphous materials, nanovoids are usually present in a-Si [2-4]. Since they are empty spaces they bring about density reduction, which can change the refractive index, electronic defect states [1] and inhomogeneous stress distribution if filled with H [5] or if they form Si-H platelets [6]. According to Refs. [7] and [8], voids and related H bonding configurations are also involved in the Staebler-Wronsky effect [9], i.e. degradation of the hydrogenated a-Si properties upon illumination. The voids are most crucial if they are large enough to accommodate H molecules [1]. In such a case, in fact, hydrogen may desorb as H₂ with the consequent reconstruction of dangling bonds and Si-Si weak bonds which causes deterioration of the electronic properties [1]. Here we report on the generation of surface blisters from nanovoids in hydrogenated a-Si layers grown by RF sputtering and later annealed. It is argued that the generation is assisted by changes of the H bonding configuration caused by the annealing.
2. Experimental

The 400 nm thick a-Si layers were deposited by RF sputtering on (100) Si substrates in Ar atmosphere at the rate of 6.3 nm/min. Different degrees of hydrogenation were achieved by introducing H into the sputter chamber at the flow rates of 0.4, 0.8 and 1.5 ml/min corresponding to an effective H density of 10.8, 14.7 and 17.6 at.%, respectively, as determined by ERDA (elastic recoil detection analysis). The samples were annealed in high purity (99.999%) Ar at 350 °C for 1 and 4 h. Investigations were performed by atomic force microscopy (AFM) and by Fourier transform infrared (FTIR) spectroscopy by employing a Bruker Tensor 37 spectrometer with 2 cm$^{-1}$ resolution. FTIR was employed to determine the type of bonding configuration of H to Si by detailed analysis of the stretching mode absorption. The integrated intensity of the absorption peaks contributing to the stretching vibration is used to follow the changes of concentration of the corresponding (SiH) bonds since such intensity is proportional to the absolute concentration apart from a constant [10,11].

3. Results and discussion

Fig. 1 is a typical AFM image of the surface of the hydrogenated a-Si layers after annealing showing the presence of blisters with size of the order of 150-220 nm and height a few nm. Their density and size increase with increasing annealing time and H content.

![Figure 1. AFM image of surface blisters in the sample hydrogenated at 0.4 ml/min and annealed for 4 h (scan area 5 μm × 5 μm).](image)

![Figure 2. IR absorption spectra in the stretching mode range for the a-Si layer hydrogenated at 1.5 ml/min non-annealed (solid curve) and annealed at 350 °C for 1 h (dash curve) and 4 h (dot curve).](image)

The set of IR spectra of Fig. 2 shows the typical shape of the stretching mode absorption as a function of the annealing time $t$ as observed for all the samples. By gaussian deconvolution applied to the spectra two peaks can be
identified at $\sim 2000$ and $\sim 2100$ cm$^{-1}$, respectively. According to literature, the $\sim 2000$ cm$^{-1}$ vibration is due to isolated Si-H mono-hydride bonds while the $\sim 2100$ cm$^{-1}$ one is ascribed to (Si-H)$_n$ clusters and to polymers, such as Si-H$_2$ dihydrides or chains of them (Si-H$_2$)$_n$, n $\geq$ 2 [2,10-12]. Upon annealing, the mono-hydride bonds break and their density decreases while the polyhydride density increases and becomes even greater than the monohydride one for H flow rate of 1.5 ml/min. This is summarized in Fig. 3 that gives $I_{2100}/I_{2000}$ as a function of $t$ for the three hydrogenation rates, with $I_{2100}$ and $I_{2000}$ to be the integrated intensity of the absorption peaks at 2100 and 2000 cm$^{-1}$.

Since the polymers reside on the surfaces of voids [2,10-12], which are usually present in a-Si [2-4], the increased density of the polymers after annealing (Figs. 2 and 3) would thus suggest that the size of the nanovoids has increased to accommodate more polymers with respect to the non-annealed state.

Fig. 2 also shows that the total integrated intensity, i.e., the total H concentration of bonded H of whichever type, decreases with increasing $t$ which indicates that annealing causes the irreversible break of some H bonds to Si. H release from isolated mono-hydrides is expected to be less likely as they represent the deepest binding sites [13]. The polymers decorating the walls of the voids have instead a smaller binding energy [13] and are expected to easily liberate their H into the voids themselves where H atoms may react to form molecular H$_2$ (Fig. 4).

The molecular H$_2$ in the gas state inside the nanovoids expands upon annealing with consequent increase of the volume of the nanovoids, which would favour their coalescence leading to bigger and bigger voids. Such bigger voids offer larger inner surfaces for the formation of additional polymers which will further contribute to the release of additional H to be transformed into H$_2$. 

![Figure 3. Plot of $I_{2100}/I_{2000}$ as a function of annealing time for the 3 hydrogenation levels.](image-url)
Eventually, the voids will reach such a big size to cause a localized lift off of the layers with the formation of surface blisters as observed by AFM. The blisters have thus developed from nanoscopic voids, decorated by (Si-H$_2$)$_n$ complexes, $n \geq 1$, which have increased their volume because of the increase of the inside pressure due to the thermal expansion of H$_2$ gas upon annealing.

**Acknowledgments**

The work has been supported by the Scientific Cooperation Agreement between CNR (Italy) and MTA (Hungary) under the contract MTA 1102 as well as by OTKA grants Nos. K-67969, NF 101329 and CK80126.

**References**