

Deposition of Si:H thin films on transparent and conductive ZnO at boundary parameters of PECVD if Sn as catalyst element is used

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Abstract: Research of convenient silicon thin film structures for solar cells with higher solar energy conversion is in area of high interest. In this paper we focus on the fabrication and study the properties of Si:H thin film which was formed on the transparent conductive thin film ZnO. We study a possibilities how to deposit by PECVD technique with assistance of catalytic effect of Sn an optimal structure of Si:H thin film /amorphous + microcrystalline + eventually with contain of Si nanowires/.

Keywords: Si:H thin film, ZnO, PECVD, catalytic effect, VLS, Si-NWs

1. Introduction

According to many published results the deposition temperature for high quality amorphous or microcrystalline silicon (a-Si:H or μ c-Si:H) is between 200 and 300 °C [1,2,3]. Up to now this area of deposition conditions was studied in detail already and it seems here it is not much more to improve. But a new form of silicon – “silicon nanowires” (Si-NWs) which can be formed by catalytic process [4,5] have got a different properties which can be used for a production of optoelectronic devices. Usually the growth of Si-NWs is stimulated by catalytic process at high temperatures/ higher than 550°C/. When the temperature is lower, the catalytic effect of some elements as Au, Ag, Al, Sn disappears. But if we replace standard chemical vapour deposition (CVD) by plasma enhanced CVD (PECVD) we can extend the growth of Si-NWs down up to about 250 °C [6,7]. For those temperatures we study an influence of the other parameters of PECVD. Our effort is focused on dilution of Silane by Hydrogen or Helium and at the same time we study effect of frequency by which the glow discharge is stimulated. When we apply only these changes we can deposit Si:H thin film with quite different quality. For a purpose of photovoltaic devices /solar cells/ we use a transparent and conductive ZnO [8] deposited on Corning glass substrate. As a convenient element for catalytic effect we chose Tin (Sn) which does not create deep impurity levels in Si as it is possible at the case of the Gold (Au).

2. Experimental

The Corning glass substrate was cleaned by solution of ethanol, then HF acid for 10 seconds and in the end by acetone. Then substrates were put into the main chamber for DC magnetron sputtering of ZnO thin film. The schematic diagram of configuration is on the picture 1.

We use unbalanced magnetron system for deposition of ZnO thin film. Magnetron system was arranged with target perpendicular to substrate. This configuration helps avoid a negative ions beam and improves a quality of deposited ZnO thin film. Conditions prepare ZnO thin films are described in table 1.

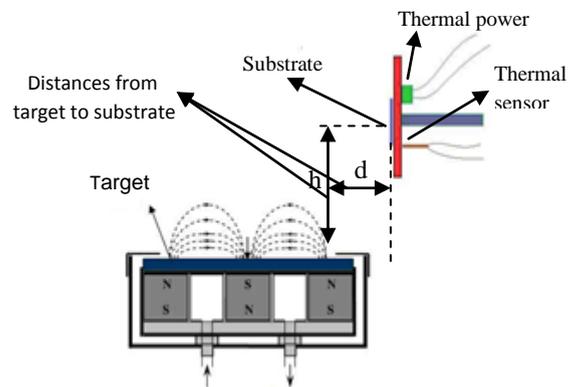


Figure 1. Schematic diagram of DC magnetron for ZnO sputtering

T ⁰	P	h	d	V	I	t	Target
200 [°C]	0,4 [Pa]	4 [cm]	2.5 [cm]	500 [V]	0.2 [A]	30 [min]	ZnO pure 99%

Table 1. The deposition conditions for ZnO sputtering

The properties (transparency and conductivity) of ZnO thin films are suitable for our aims. The thickness of ZnO thin film on the substrate is about 400nm, resistivity about 20 Ω cm. For the deposition of 7nm catalytic Sn layer we use SenVac apparatus. Sn was evaporated and deposited with deposition rate 0,2 nm/s. To form the nanoparticles, the samples were heated up to about 260 °C (about 12 h) and in the environment of hydrogen plasma enhanced at frequency 13.56 MHz treated 2 minutes. PECVD system was used to create Si:H film by decomposition of standard precursor – SiH₄. The crystallographic structure of Si:H thin films was formed in two different environments, Silane diluted by Helium or Hydrogen. In both cases the influences of temperature (220, 260 and 300 °C) and frequency (13.56, 54.24 and 108.48 MHz) we studied.

Before the deposition Si:H thin film /see the deposition condition at Table 2./ the ZnO surface was coated by Sn

ultrathin film. For our experiments we chose the thickness 7nm. During annealing at 250 °C we apply treatment at frequency 13.56 MHz for H2 plasma excitation. By this way we create convenient size of Sn nanoparticles. For the thickness measurement we use stylus method and calculated deposition rate. The structure of the Si:H thin film was determined by Raman spectroscopy, the topography by Scanning Electron Microscopy (SEM).

Parameter	Helium	Hydrogen
Temperature	220 °C	220 °C
Time	14 minute	14 minute
Frequency	13.56 MHz, 54.24 MHz, 108.48 MHz	13.56 MHz, 54.24 MHz, 108.48 MHz
Rate gas	50:1 (He:SiH ₄)	50:1 (He:SiH ₄)
RF Power	4 W	4 W

Table 2. Synthesis conditions of Si:H thin films

3. Result and discussion

On the figure 2a is typical ZnO thin film while the figure 2b shows Sn nanoparticles on ZnO surface, both measured by SEM.

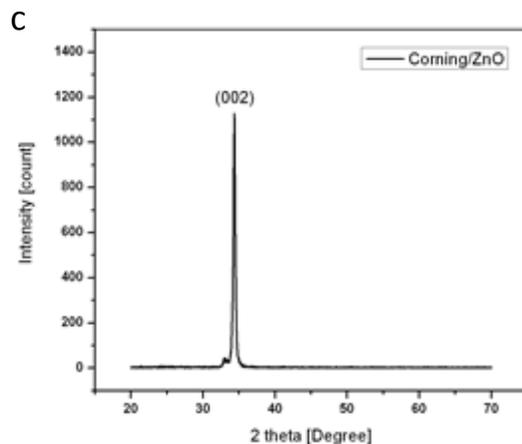
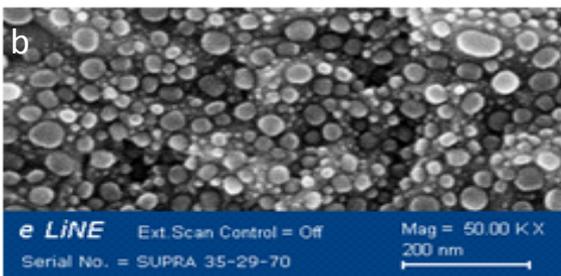
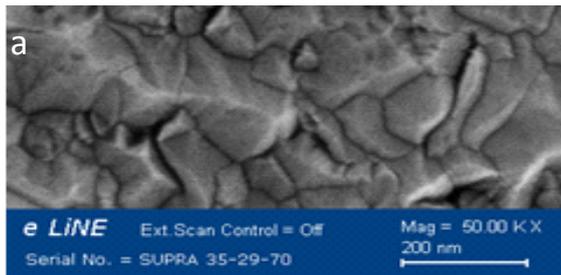


Figure 2: a) Morphology of ZnO nanoparticles
b) Sn on ZnO after annealing and H2 plasma treatment
c) XRD spectroscopy of ZnO thin film.

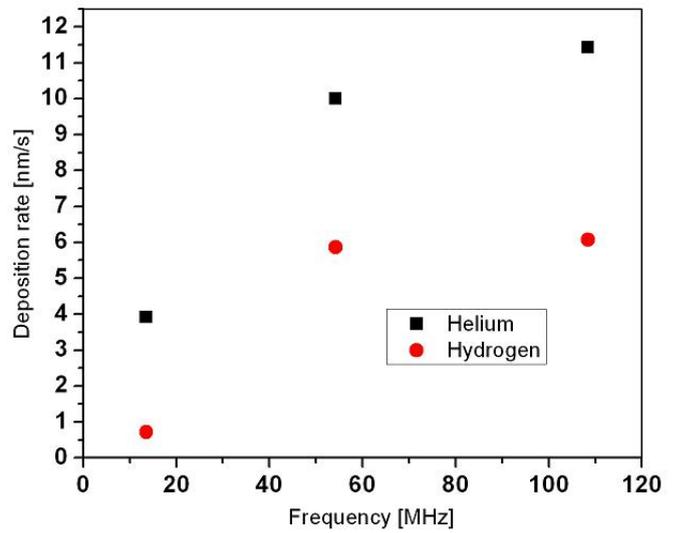


Figure 3. Deposition rate of Si:H thin films in Hydrogen (black squares) or Helium (red circles) plasma at difference frequencies.

Figure 3 shows deposition rate of the Si:H thin film for different dilution gases – Hydrogen and Helium. The deposition rate of the Si:H thin film in the Helium plasma is higher than if the Silane is diluted by the Hydrogen. Similarly the deposition rate of the Si:H films also depends on the frequency for plasma enhancement and it is higher with increasing frequency. Besides it, we can see the role of the Sn metal catalyst for the formation of the thin film surface. Without Sn, there are no Si NWs. Due to high dilution of Silane the deposition rate and eventual growth of Si NWs is very low, VLS process is not extremely quick but under control of deposition parameters. Figure 4 shows the surface morphology of the thin film if the Sn-NPs was or was not used at temperature 220 °C and frequency 13.56 MHz.

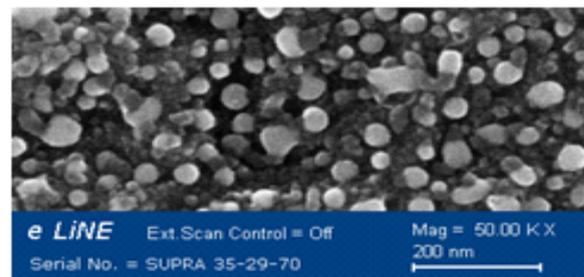


Figure 4. Thin film face morphologies which was deposited without a) and with b) Sn catalyst. The surface deposition temperature is 220 °C and plasma enhanced frequency is 13.56 MHz

The Si:H surface changes when the frequency increases from 13.56 MHz to 108.48 MHz in both environments Hydrogen and Helium. That we show in Figure 5. Size and density of the catalyst nanoparticles change with the change of frequency. When we apply higher frequency, the VPL process of Si-NWs at deposition temperature 220 °C disappears. But what is interesting the crystallinity of Si:H thin films increases while the amorphous phase is on the decrease. Quite different is the structure of Si:H if the Silane is decomposed at Helium plasma. Here the role of frequency is not noticeable, only deposition rate increases.

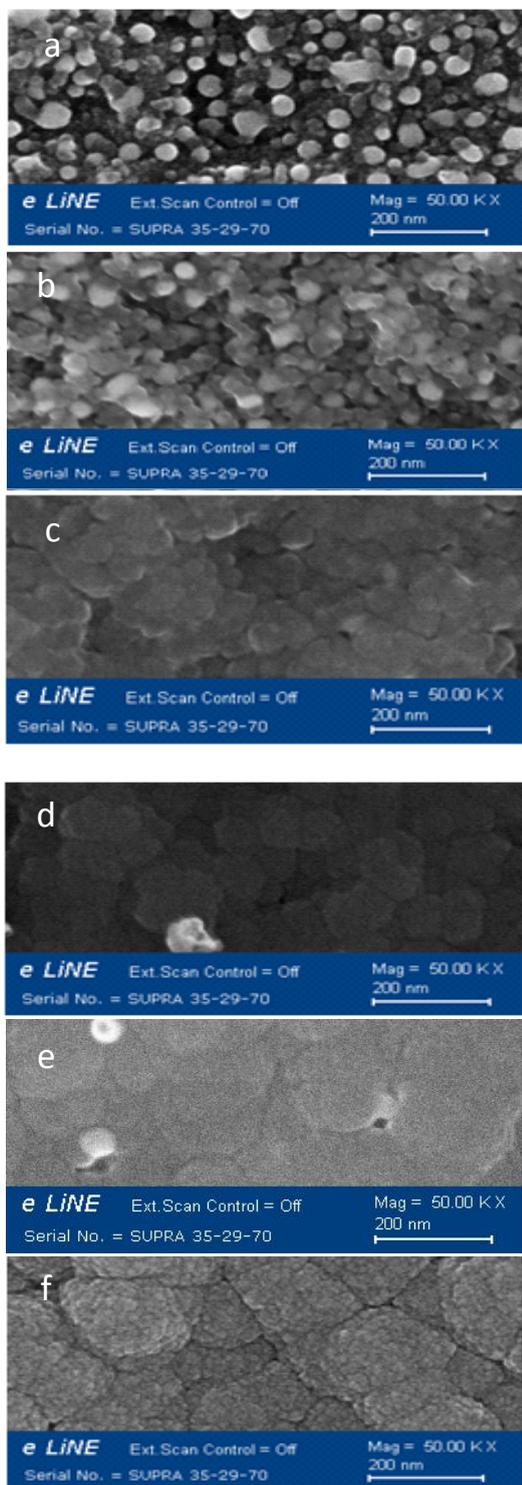


Figure 5. Morphology of Si:H deposited in the Hydrogen (a, b, c) and Helium (d, e, f) glow discharge. The plasma frequency 13.56 MHz was applied in case of a) and d), 54.24 MHz for b) and e), 108.48 MHz for c) and f).

The results from Raman spectroscopy are on the following Figure 6. In case of depositions in hydrogen rich atmosphere highly crystalline films were grown (Fig. 6 a). This is given by etching effect of hydrogen, when amorphous material is removed easier than the microcrystalline counterpart. Depositions in helium plasma lead to amorphous structure, because there is no enhancement of the microcrystalline growth (no etching effect).

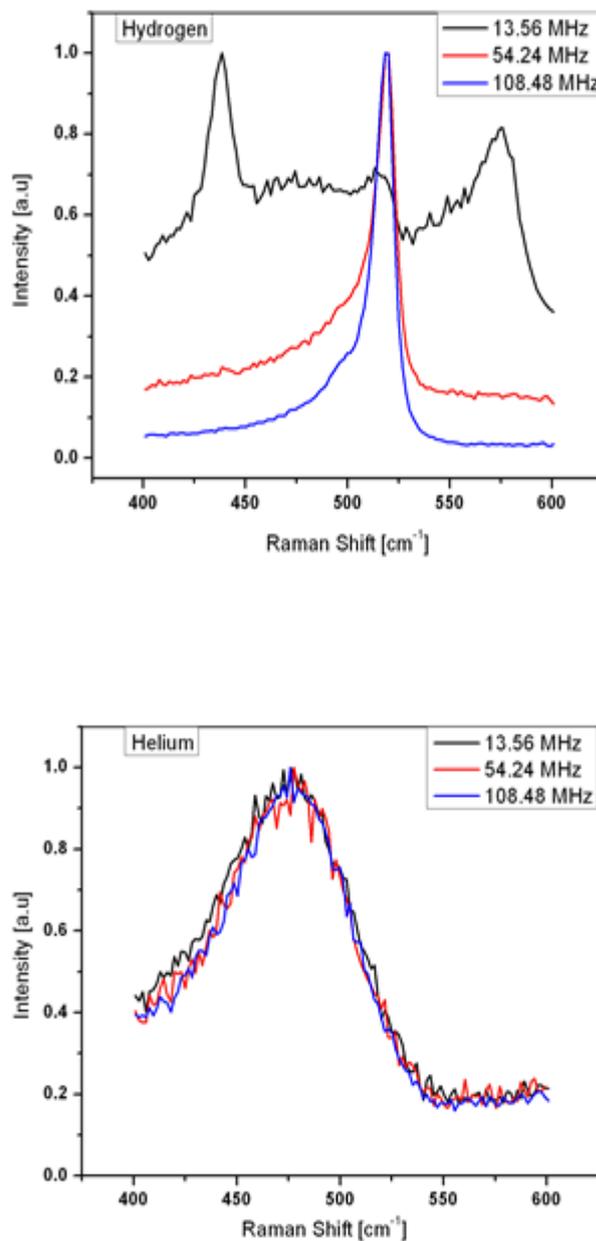


Figure 6. Raman spectroscopy of Si:H thin film at different frequencies in Hydrogen or Helium plasma

The Raman spectra of the sample deposited in hydrogen at 13.56 MHz exhibit two prominent bands at 425 and 575 cm^{-1} . These two peaks are the signature of the under lying ZnO substrate. Substrate is visible even for this in silicon highly absorbed excitation wavelength (442 nm) thanks to the very low thickness of the deposited film.

4. Conclusion

Our work is focused on the boundary conditions of PECVD process which we can use for growth of Si-NWs. Low temperature and convenient structure of silicon thin films with good optical and electrical properties of Si:H thin film are required for to solar cell application. We can conclude that the Hydrogen plasma in comparison with Helium plasma leads to growth of highly crystalline Si:H thin films. We have demonstrated the important effect of frequency for glow discharge excitation also. In both cases /H₂ or He plasma/ with the increasing frequency the deposition rate increases, in case of H₂ the crystallinity increases also. It is surprising that according to the SEM pictures in this case the silicon NWs vanishes. In case of He plasma the deposited films are fully amorphous, but their relatively rough structure made them as perspective for higher absorption of light. We consider these forms of thin silicon films interesting for solar cells applications.

5. Acknowledgements

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