Proc. Int. Conf. and Summer School on Advanced Silicide Technology 2014
JJAP Conf. Proc. **3** (2015) 011302

The Laser Ablation as a perspective technique for the deposition of metal-silicide nanoparticles in situ embedded in PECVD of Si:H thin films

The Ha Stuchlikova[1*], Radek Fajgar [2*], Martin Kostejn[2], Vladislav Drinek[2], Zdenek Remes[1,3], Jiri Stuchlik[1*]

[1] *Institute of Physics ASCR, v. v. i., Cukrovarnická 10/112, 162 00 Praha 6, Czech Republic*

[2] *Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Rozvojová 135, 165 02 Praha 6, Czech Republic*

[3] *Czech Technical University in Prague, Faculty of Biomedical Engineering, Sitna 3105, 27201 Kladno, Czech Republic*

E-mail: hotheha@fzu.cz, fajgar@icpf.cas.cz, stuj@fzu.cz

(Received August 1, 2014)

In this paper we introduce amorphous hydrogenated silicon thin films (a-Si:H) deposited by PECVD with embedded magnesium silicide (Mg_2Si) nanoparticles (NPs) which are created by Reactive Laser Ablation (RLA) of Mg target in low pressure of silane (SiH_4). Both techniques are periodically changed in short intervals – each of the monolayers of Mg_2Si NPs is covered by thin a-Si:H film. The physical characteristics of those films are studied not only on high quality optical substrates but in diode structures too. As a final result we introduce the voltage dependence of the electroluminescence of deposited diodes.

1. Introduction

The Laser Ablation (LA) is a convenient technique for the deposition of nanoparticles of different materials by laser induced evaporation of targets. Some compounds can be deposited by Reactive Laser Ablation (RLA). Especially the semi-conductive silicides such as Mg_2Si represent a group of materials for which this technique is suitable [1,2].
The Plasma Enhanced Chemical Vapour Deposition (PECVD) is a widely used technique for the deposition of thin films with very different qualities. The long-time effort is focused on the group 14 of the periodic table of elements, i.e. C, Si, Ge (convenient precursors CH_4, SiH_4 and GeH_4) and their eventual alloys. The properties of those thin films incorporated in different structures have already found large usage in numerous applications. But for further effective application it is necessary to modify and improve their quality.
In our previous work [3,4] we have already demonstrated the formation of cubic Mg_2Si nanolayers or nanoclusters and their integration within the structure of hydrogenated silicon thin films (Si:H) by *ex situ* methods. In this paper we demonstrate a simple vacuum system for the combination of both methods for the preparation of nanocrystalline Mg_2Si NPs which are embedded *in situ* in the a-Si:H matrix. For the deposition of Mg_2Si NP, the Laser Ablation technique is generally useful using a Mg_2Si target. In our case we have used elemental magnesium target and its reactive ablation at low pressure of silane. This technique affords the NPs of the requested size. The Raman spectra of the deposited thin film structure, its optical properties and perspectives for applications are studied and discussed.

2. Experimental methods

The PECVD with standard 13.56 MHz Radio Frequency at two electrodes configuration was used for the stimulation of mini-glow discharge and the decomposition of silane under the pressure of 12 Pa, with 5 W power and the substrate temperature of 200 °C. These conditions are quite convenient for the deposition of standard quality a-Si:H thin films.
The Mg_2Si nanoparticles were grown by Reactive Laser Ablation. A magnesium target was irradiated by 6000 pulses of focused beam of the ArF excimer laser with energy 55 mJ/pulse at the wavelength of 193 nm. The distance between the target and heated substrates was set to about 3 cm and the pressure of silane was 2 Pa. For the *in situ* alternation of both the different deposition techniques we constructed a special deposition chamber (see the Fig. 1).
The Raman spectra of the grown samples were measured using Nicolet Almega XR dispersive spectrometer with excitation 473 nm. High resolution transmission electron microscopy (HRTEM) was conducted on a JEM 3010 microscope (JEOL), operated at 300 kV (LaB6 cathode, point resolution 1.7 Å) with an energy dispersive spectrum (EDS) detector attached. The images were recorded on a CCD camera (Gatan) with 1024x1024 pixels resolution using the Digital Micrograph software package.

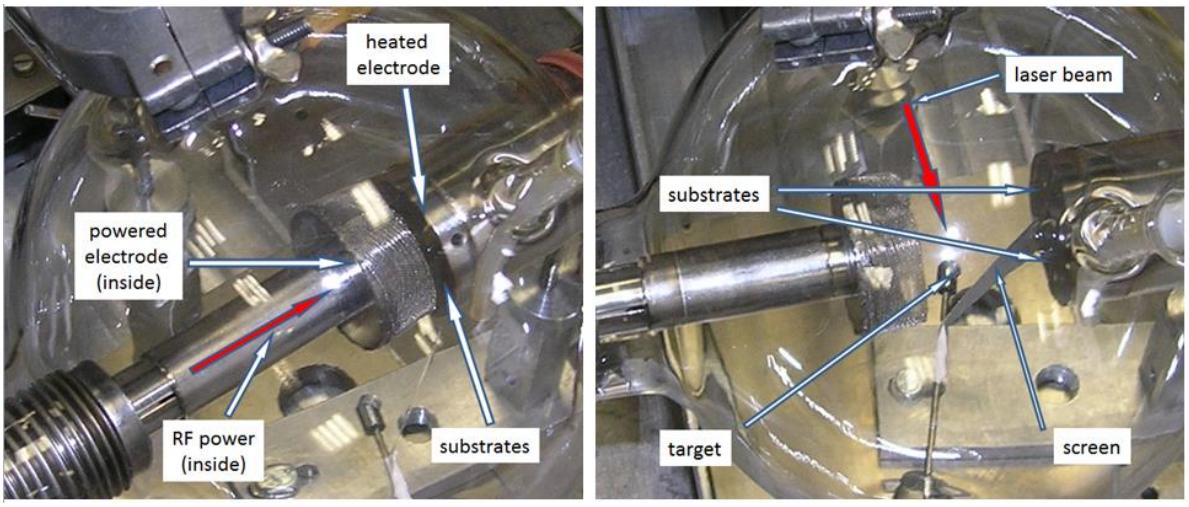

Fig. 1. Deposition chamber for *in situ* deposition at condition PECVD and RLA
- Left picture - position of electrodes for PECVD deposition
- Right picture - position of target for RLA deposition

The temperature dependence of the DC dark electrical conductivity was made using Keithley 237 High voltage source measure unit equipped with Peltier/water cooled and electrically heated vacuum stage operating in the temperature range 250 – 400K. The optical absorbance was measured in a wide spectral range in the visible and near infrared region using the constant photocurrent method (CPM) and photothermal deflection spectroscopy (PDS). CPM is based on measuring the amplitude modulated (mechanical chopper at 10 Hz) light intensity keeping the ac photocurrent constant. 150 W halogen lamp with Horiba H20IR monochromator (600 gr/mm) was used as a light source. The photocurrent was measured by a lock-in amplifier referenced to the frequency of the amplitude modulated monochromatic light. The light intensity was monitored by a PbS detector.

3. Results and discussion
3.1 Results

By the *in situ* techniques mentioned above we deposited two structures (A and B) for comparison. The structure A is formed by a-Si:H/Mg_2Si/a-Si:H whereas the structure B consists of only two depositions of a-Si:H without Mg_2Si NPs. First, PECVD was used to grow an a-Si:H layer on the Corning glass 7059 substrates at the temperature of about 180 °C. The positions of the powered electrode for stimulation of glow discharge in silane and the target for LA were then changed. Laser ablation of the magnesium target was performed and Mg_2Si NP were formed in the gas phase by the interaction of the ablated magnesium atoms/clusters with SiH_4. Mg_2Si NPs were covered by the a-Si:H thin film using the same conditions as mentioned above.
While the deposited a-Si:H thin layers without NPs are very smooth, homogeneous and standard quality thin films, the structure A is noticeably rougher, as expected.

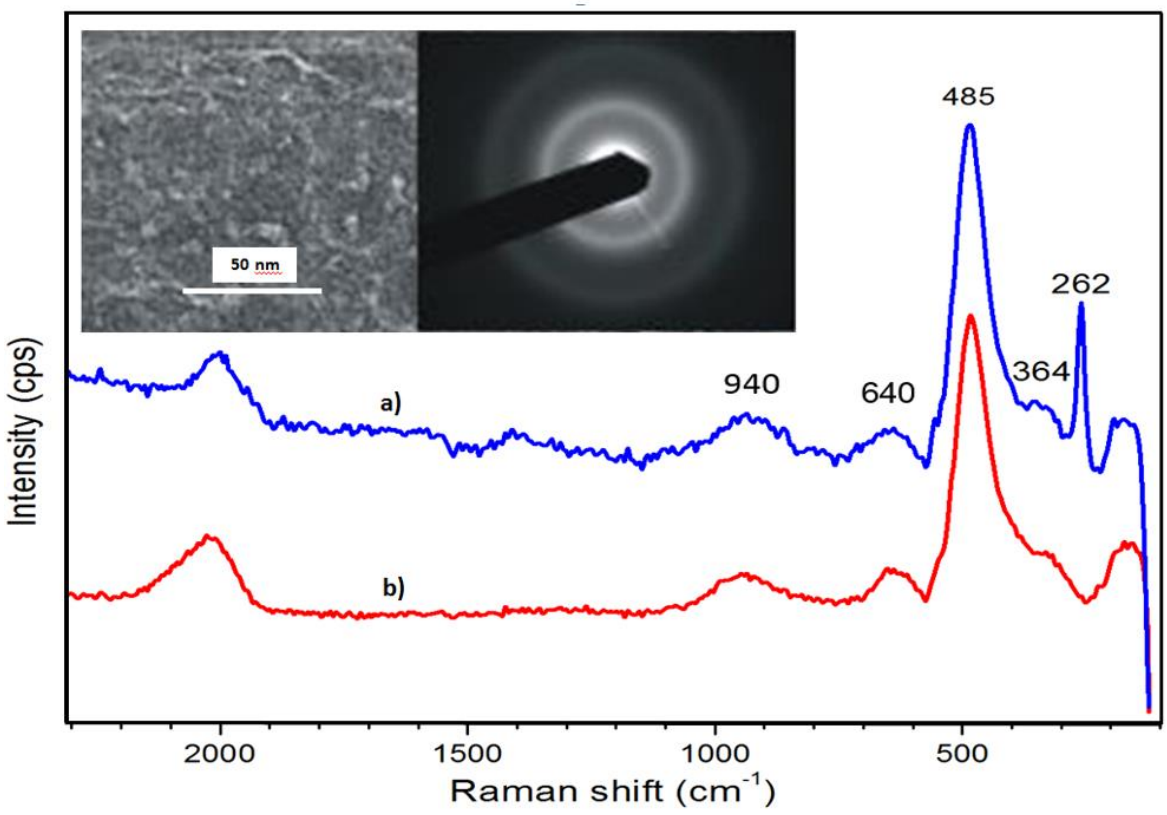

Fig. 2. Raman spectra of the deposited films, structure A, a-Si:H/Mg_2Si/a-Si:H film (a) and structure B, only a-Si:H layer (b). Left inset: HRTEM image of the deposited structure A, Right inset: corresponding selected electron diffraction pattern.

The Raman spectra (Fig. 2) show the most intense peak centered at 485 cm^{-1} which is typical for amorphous silicon. Second harmonic of this intense band is present as a broad feature centered at about 940 cm^{-1}. There is no peak attributable to crystalline silicon, located at about 520 cm^{-1}, which proves completely amorphous structure of the silicon matrix. The strong and narrow band centered at

262 cm^{-1} is observed and together with a weaker and wider band at 364 cm^{-1} belongs to Mg_2Si cubic structure [5, 6]. The broad bands centered at about 640 cm-1are attributed to the deformation vibrations of the amorphous silicon hydride and multiphonon structure. Corresponding valence vibration of Si-H structures is visible as broad bands above 2000 cm^{-1}.
HRTEM imaging shows the film is transparent and sintered from nanoparticles of 10-20 nm size (Fig. 2, left inset). The crystallites were small (up to 5 nm) and electron diffraction revealed diffusion rings (Fig. 2, right inset) typical for crystallites of this size embedded in amorphous matrix. Cubic Mg_2Si NPs were recognized in the diffraction pattern using the software package.
To characterize the quality of the deposited thin films we performed both the above mentioned deposition processes for 30 times. Titanium electrodes were then deposited on the prepared multilayered thin films using *ex situ* coplanar configuration and electrical and optical quality of the samples were measured. On the Fig. 3a we introduce the temperature dependence of specific electrical conductivity (measured at dark) σ_{DC} and the absorption coefficient α as a function of energy of photons, measured by the CPM method (Fig. 3b).

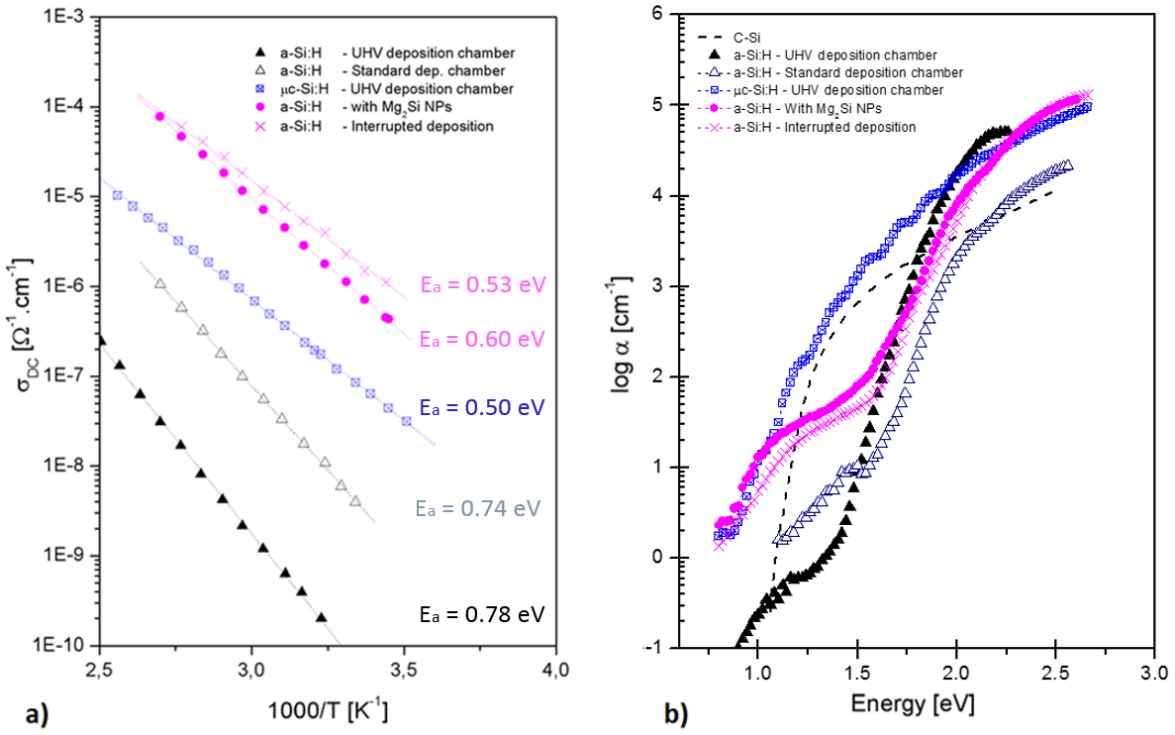

Fig. 3. Temperature dependences of electrical conductivity of the deposited thin films (a) and absorption coefficient as a function of energy of photons of a-Si:H thin films deposited at different conditions (b)

3.2 Discussion

To compare the electrical and optical quality of the a-Si:H thin layers grown in the simple glass deposition reactor used for in-situ nanoparticle embedding, we have measured the temperature dependence of dark coplanar conductivity and evaluated the activation energy, and we also measured the absorption coefficient by the CPM method. In the case of UHV chamber after good degassing and

if high purity silane (99.9999%) and hydrogen (99.99999%) are used, the electrical dark conductivity $\sigma_{DC,}$ and the absorption coefficient α (in the range of energies between 1.0 and 1.5 eV) are low, and the activation energy E_a is high (0.78 eV - see the black triangles in the graphs a) and b)) When we deposit the a-Si:H thin film in the glass chamber, the level of defects increases, the electrical dark conductivity increases too and the activation energy E_a decreases a little to the value of 0.74 eV. It is known that the level of oxygen is higher in the glass chamber, and the band gap of a-Si:H is higher too. In this conditions the PECVD process was interrupted and during this time Mg_2Si NPs were deposited on some of the substrates by the RLA process. To observe the effect of NPs, some samples were left without NPs, i.e. the deposition process was only interrupted.
Comparing the optical absorption coefficients of the high quality a-Si:H and the a-Si:H with the *in-situ* embedded nanoparticles, we observe a significant increase of the optical absorption in the sub-band gap region 0.8 – 1.5 eV related to the conductivity band tail below the optical absorption edge. This increase of the optical absorption is related to the increase of the localized state density, partly due to the presence of the nanoparticles and partly due to the increase of the defect density in the intrinsic a-Si:H. The E_a decreases to the value of 0.6 eV for the thin film with embedded Mg_2Si NPs and to the value of 0.53 eV for thin films deposited by interrupted process. In this case the effect of embedded NPs is not so pronounced. For a complete comparison we added the data of microcrystalline silicon µc-Si:H deposited in UHV chamber and with high purity gases. While the temperature dependence of σ_{DC} is not so different, the CPM measurement shows that the character of the thin film is quite different.

4. Conclusions

For the first time the combination of PECVD of a-Si:H thin films and Reactive Laser Ablation of magnesium target in low pressure of silane have been used for the preparation of Mg_2Si NPs which are *in situ* embedded in the a-Si:H matrix. The Mg_2Si cubic structure has been confirmed by the Raman spectroscopy and electron diffraction techniques and crystalline size of Mg_2Si NPs where evaluated from HRTEM. Although we compare the basic physical parameters (α, $\sigma_{RT,}$ E_{act}) of the deposited thin films from two different deposition systems (standard vacuum and UHV deposition system), we demonstrate that the a-Si:H thin films modified by *in situ* embedded Mg_2Si NPs has similar quality as microcrystalline silicon thin films. The optimization of multilayer structures and perspectives of application are subjects of further study.

Acknowledgments

The work was performed with LH12236 (MSMT KONTAKT II, Czech Republic)

References

[1] R.G. Morris, R.D. Redin, G.C. Danielson. *Physical Review* 109 (1958) 1909.
[2] D. Tamura, R. Nagai, K. Sugimoto, H. Udono, I. Kikuma, H. Tajima, I.J. Ohsugi. *Thin Solid Films*. 515 (2007) 8272.
[3] N.G. Galkin, K.N. Galkin, I.M. Chernev, R. Fajgar, T. H. Stuchlikova, Z. Remes, and J. Stuchlik, *Phys. Status Solidi C* 10 (2013) 1712 – 1716
[4] T.H. Stuchlíková, J. Stuchlík, Z. Remeš, R. Fajgar, N.G. Galkin, K. N. Galkin, I. M. Chernev , NANOCON 2013, 5th In-ternational Conference, October 16th - 18th 2013 Hotel Voronez I, Brno, Czech Republic, EU
[5] P.H. Baranek, J. Schamps, I. Noiret. *J. Phys. Chem*. B 101, 9147 (1997).
[6] K.N. Galkin, A.M. Maslov, V.A. Davydov. *J. Appl. Spectroscopy* 73, 204 (2006).