

NEAR INFRARED PHOTOLUMINESCENCE OF THE HYDROGENATED AMORPHOUS SILICON THIN FILMS WITH IN-SITU EMBEDDED SILICON NANOPARTICLES

#ZDENĚK REMES*,**, JIŘÍ STUHLÍK*, ADAM PURKRT*, MARTIN LEDINSKÝ*, JAROSLAV KUPČÍK***

* *Institute of Physics CAS CR, Cukrovarnická 10, 162 00 Prague 6, Czech Republic*

** *Faculty of Biomedical Engineering CTU in Prague, Nam. Sitna 3105, Kladno, 272 01, Czech Republic*

*** *Institute of Inorganic Chemistry CAS, Husinec-Rez c.p. 1001, 25068, Czech Republic*

#E-mail: remes@fzu.cz

Submitted September 2, 2016; accepted December 7, 2016

Keywords: Amorphous silicon, Chemical vapor deposition, Photothermal deflection spectroscopy

The intrinsic hydrogenated silicon layers with embedded silicon nanoparticles were grown in-situ at 250°C on glass substrates by the radio frequency plasma enhanced chemical vapor deposition (CVD) from silane highly diluted in hydrogen. The changes in the optical absorption coefficient were detected by the photothermal deflection spectroscopy (PDS). The transition from amorphous to crystalline phase for samples deposited at 5 - 6 % silane concentration correlates to the crystalline volume fraction about 50 % as detected by Raman spectroscopy and the high resolution transmission electron microscopy (HRTEM). The room temperature photo-luminescence increases significantly with increased crystallinity volume fraction but diminishes abruptly when crystallinity volume fraction exceeds above 80 %. The photoluminescence intensity strongly correlates with the presence of isolated silicon nanoparticles in the mixed amorphous and crystalline phase. The strongest photoluminescence was found in the sample with mixed phase of amorphous matrix and isolated silicon nanoparticles and the crystalline volume fraction about 50 %.

INTRODUCTION

The large area p-n junctions and diodes with rectifying current-voltage characteristic are deposited in the form of thin films by plasma enhanced chemical vapor deposition (PECVD). Both n-type as well as p-type doping are easily achievable in the hydrogenated amorphous silicon (a-Si:H) with applications in large area electronic devices such as solar cells, TV screens and scanners [1]. Moreover, the large area and low cost near infrared electroluminescence panels based on a-Si:H may represent a new application for amorphous silicon in markets like night vision and security. Nanoparticles (NPs) embedded in the hydrogenated amorphous silicon (a-Si:H) open the opportunity for a new nanocomposite semiconducting material suitable for low cost, large area energy conversion applications. The concept of embedding NPs into amorphous matrix may result in an increase of the efficiency of energy conversion in solar cells and LEDs due to the extended spectral sensitivity in the NIR [2].

The embedding of NPs into a-Si:H is a difficult task that need to focus on the quality of the NP surface and NPs/a-Si:H interface to reduce the defect states and enhance the injections of free carriers into NPs by reducing the non-radiative recombination centers. In our previous papers we have investigated a-Si:H layers

and thin film diodes with the embedded NPs. The most simple way how to integrate NPs into a-Si:H thin films was the interruption of PECVD deposition process to deposit NPs dispersed in liquid *ex-situ* by the “drop and dry” method leading to macroscopic inhomogeneity in the surface coverage [3]. Another disadvantage of the vacuum process interruption was the oxidation or contamination of the surface by organic residue when exposed to air. Therefore, we have switched to the *in-situ* techniques such as reactive deposition epitaxy (RDE) [4], laser ablation [5] and the magnetron sputtering followed by plasma treatment [6]. The *in-situ* formation of silicide NPs by RDE and laser ablation was confirmed by the Auger electron spectroscopy (AES) and electron energy loss spectroscopies (EELS) and by the optical absorbance and Raman spectroscopy [7]. The homogeneous coverage of a-Si:H surface by vacuum evaporated and hydrogen plasma treated Mg₂Si NPs with diameter below 10 nm was confirmed by the scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) [8]. Recently we published the paper showing that the silicide NPs embedded in amorphous silicon matrix by solid phase epitaxy enhance the light absorption in the near infrared region [9].

The integration of the highly luminescent silicon NPs into a-Si:H thin films gave promising results [10]. Recently, low dimensional silicon photonics emerged,

with the delicate interplay between the silicon and the embedding matrix that allows underpinning new phenomena [11]. We participated in the determination of the absorption cross-section of silicon nanocrystals [12]. In this paper we show the new results on series of silicon layers deposited under varying hydrogen plasma dilution with the aim to create the *in-situ* silicon NPs embedded in a-Si:H during the thin film growth. The most important relation which we want to discover is relation between the near infrared photoluminescence and the structure of hydrogenated silicon.

EXPERIMENTAL

The hydrogenated silicon layers were deposited from silane SiH₄ diluted in H₂ on fused silica glass by capacity coupled 13.56 MHz radio frequency glow discharge PECVD deposition process with standard two electrodes configuration. The dilution series are summarized in the Table 1. It should be noted that a change of only one parameter for RF glow discharge and decomposition of silane is not possible to sustain the stable plasma and to deposit the layers of similar thickness. Thus, the dilution of silane is only informative, with the parameters to change being the pressure, RF power and deposition time.

The optical reflectance and absorption spectra were measured simultaneously in the broad spectral range from UV to near IR 250 - 1700 nm using the dual beam setup. The reflectance was measured as the ratio of the reflected and incident light by the compound detector based on the integrating spheres equipped with Si and InGaAs photodiodes. The absorbance spectra were measured by photothermal deflection of the probe laser beam parallel to the sample immersed into transparent liquid Fluorinert FC72. The amplitude of the deflection was proportional to the optical absorption in thin film. The absorbance was normalized by the spectrum of the highly absorbing black coating. The photothermal deflection spectroscopy (PDS) measures the absorbance down to 10⁻⁴ [13].

The steady-state photoluminescence spectra were measured at room temperature using the continuous green laser (532 nm, 50 mW) as the PL excitation energy source, the f/1 objective collecting the photolumines-

Table 1. Silane concentration, sample thickness d , rel. intensity of photoluminescence PL, crystalline volume fraction X_c and the absorp. coeff. α at 1.4 eV.

SiH ₄ (%)	d [nm]	PL [a.u.]	X_c [%]	α [cm ⁻¹]
4.0	830	0.01	81	400
5.0	800	0.4	79	600
5.5	770	0.95	57	480
6.0	870	0.66	22	16
8.0	868	0.15	0	13

cence light, the monochromator with spectral resolution 8 nm and the fW sensitivity photodiodes with AC gain 1 pA/V to detect the low intensity optical spectra in the visible and near infrared spectra range 400 - 1600 nm. The spectra were recalculated for the spectral efficiency of monochromator grating and detectors.

The Raman spectra were measured in the back-scattering geometry using micro-spectroscopic Raman setup equipped with excitation laser of 442 nm (InVia REFLEX, Renishaw). The intensity of the incident laser was reduced by neutral density filters to 12 mW in order to prevent local sample heating.

Morphological and diffraction analyses were performed on high resolution transmission electron microscope (HRTEM) JEOL JEM 3010 (Japan) equipped with a thermo emission LaB6 cathode and operated at 300 kV. Thin layers for HRTEM observations were scraped from glass substrate by a sharp scalpel. The scraped pieces were gently spread on a standard carbon coated Cu TEM grid.

RESULTS AND DISCUSSION

The optical spectra show the interference fringes related to the thin film thickness, see Figure 1 and Table 1. The fitting of the thickness has been done using the commercial thin film software FilmWizard®. The PL spectrum was digitally smoothed by taking geometric mean with the span of one interference period. The optical absorption coefficient spectra evaluated from PDS are summarized in Figure 2 and the absorption coefficient at 1.4 eV is in Table 1. The spectra can be separated into two groups: 1) the amorphous silicon-like spectra deposited under relatively high silane concentration at and above

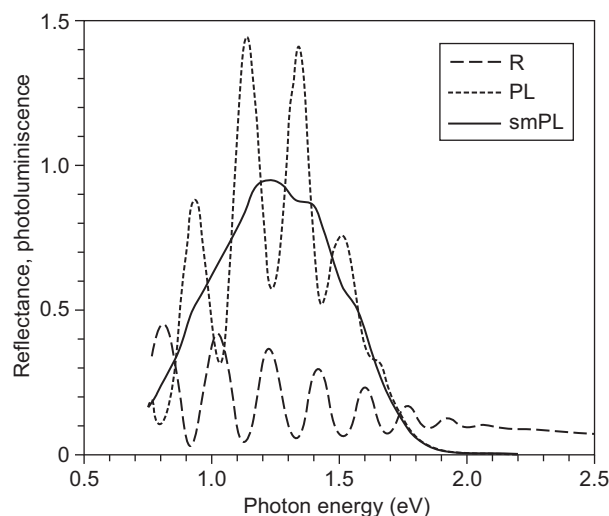


Figure 1. The reflectance and photoluminescence spectra of the hydrogenated silicon layer (sample 5.5 % silane). The interference fringes in PL spectrum were suppressed by numerical smoothing (smPL).

6 % with the absorp. coeff. at 1.4 eV below 20 cm^{-1} , and 2) the crystalline silicon-like spectra under low silane concentration below 6 % with the absorp. coeff. at 1.4 eV above 400 cm^{-1} . These observations agree well with the previously published phase evolution from the amorphous phase into the mixed and eventually microcrystalline phase depending on the hydrogen dilution [14].

The transition from amorphous to crystalline phase was also detected by Raman spectroscopy, see Figure 3. The pure amorphous structure appears in the range above 6 % silane concentration. For the dilution below 5 % silane the structure is mostly crystalline. The previous results showed by factor analysis the presence of the two and only two spectrally independent components in the

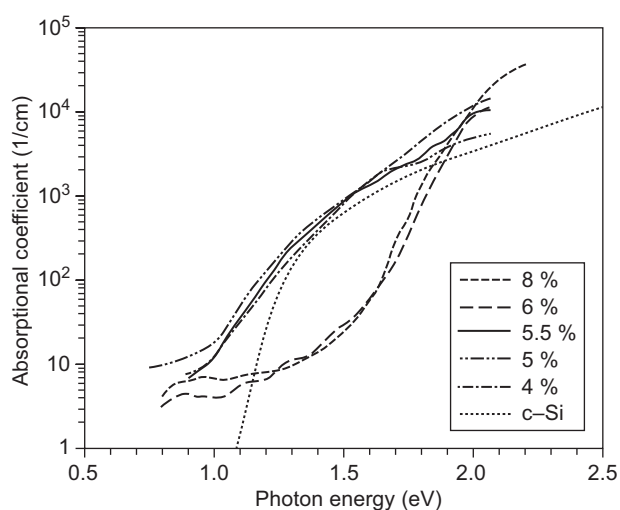


Figure 2. The optical absorption coefficient spectra of the silane concentration series of the hydrogenated silicon layers prepared by CVD. For comparison the spectra of single crystal silicon (c-Si) are also shown.

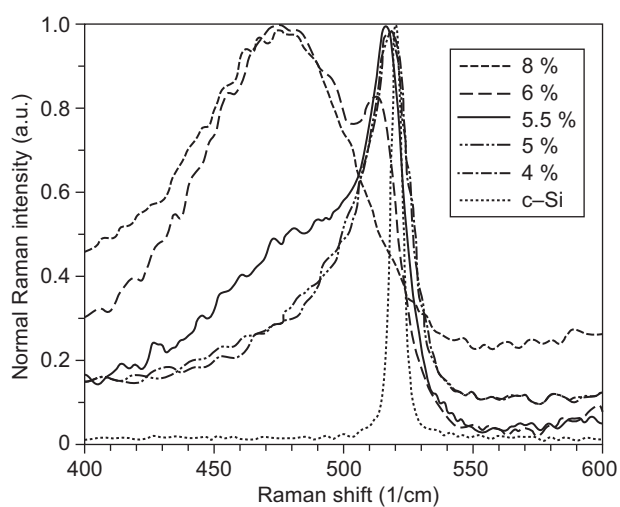


Figure 3. Raman spectra measured on the silane concentration series of the hydrogenated silicon layers prepared by CVD. For comparison the Raman spectra of single crystal silicon (c-Si) are also shown.

Raman spectra of the mixed phase [15] which means there are interesting three basic structures: amorphous with low crystalline volume fraction, microcrystalline with high crystalline volume fraction and the transient phase consisting of the insulated silicon nano-crystallites embedded in amorphous matrix. According to our results the mixed phase corresponds to the crystalline volume fraction about 50 % which appears in the sharp region between 6 and 5 % silane dilution depending on silane and hydrogen flow rates, pressure in the chamber and RF power.

The smoothed PL spectra are summarized in Figure 4. It should be noted that the green excitation light ($532 \text{ nm} = 2.33 \text{ eV}$) is highly absorbed both in amorphous as well as in the crystalline phase and the PL originates at the thin film surface. The smoothed spectra show broad band PL in near IR region with maximum at 1.2 eV. The PL of hydrogenated amorphous layers with negligible crystalline volume fraction is rather low but increases significantly with hydrogen dilution reaching maximum at 5 - 6 % silane concentration and abruptly diminishing in samples deposited at silane concentration below 5 %. The strongest photoluminescence was found in the sample with mixed amorphous/crystalline phase deposited at silane concentration at 5.5 %. The 6 % and 8 % samples with similar optical absorption coefficient have significantly different PL intensity. On the other hand the sample 4 % with negligible PL and relatively strongly luminescent 5.5 % sample have very similar absorption coefficient. We conclude that unlike the strong correlation with the crystal volume fraction evaluated from Raman spectra, the photoluminescence only partly correlate with optical absorption spectra.

The HRTEM dark field (DF) image of the sample deposited with 5.5 % silane shows the presence of silicone nanocrystals embedded in amorphous matrix. DF image, which was performed with diffracted beam

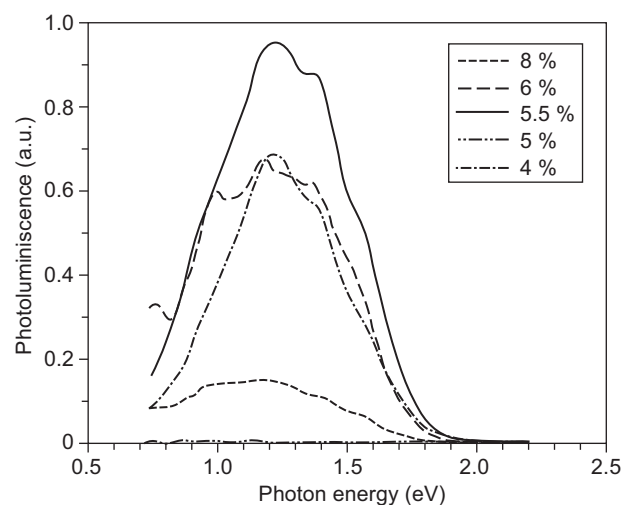


Figure 4. The comparison of the smoothed room temperature near infrared photoluminescence spectra of the hydrogenated silicon layers prepared by CVD from silane diluted by hydrogen.

corresponding to Si (1 1 1) reflection and selected by the objective aperture, shows the presence of silicon nanocrystallites with size 10 - 20 nm visible as white spots on the Figure 5. Electron diffraction pattern (Figure 5, in corner), obtained from the silicon film, consist from two types of circles: weak broad circles confirming the presence of very small nanocrystallites with size just few nm and the intensive and dominating sharp circles and spots arranged to circles confirming the presence of relatively bigger crystal silicon nanoparticles with size above 10 nm.

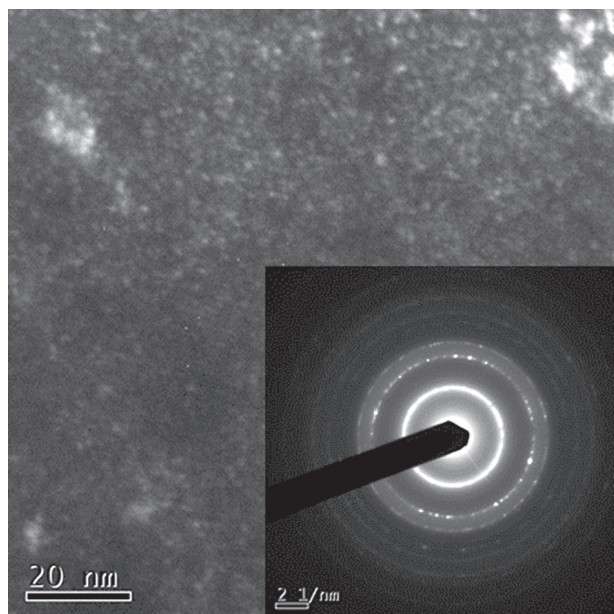


Figure 5. The HRTEM dark field image and electron diffraction pattern of silicon layer deposited with 5.5 % silane.

CONCLUSIONS

Raman spectroscopy, photoluminescence and optical absorption studies have proved to be powerful means of exploring the optical properties of localized states and the details of recombination processes in amorphous semiconductors. The near infrared photoluminescence of hydrogenated amorphous silicon with low crystallinity fraction is rather low but increases significantly with crystalline volume fraction reaching maximum at about 50 % and diminishes abruptly in samples with crystalline volume fraction above 80 %. The photoluminescence intensity strongly correlates with the presence of isolated silicon nanoparticles in the mixed amorphous and crystalline phase. The high resolution transmission electron microscopy (HRTEM) shows the presence of the isolated silicon NPs embedded in amorphous matrix in the hydrogenated silicon deposited with crystalline volume fraction around 50 %. The detailed mechanism how the enhanced photoluminescence is related to the silicon nanocrystallites is still not clear.

Acknowledgement

This work was supported by the project 16-10429J of the Czech Science Foundation and the project KONNECT-007 of the Czech Academy of Sciences.

REFERENCES

- Street R.A. (1991). *Hydrogenated amorphous silicon*. Cambridge University Press.
- Torchynska T.V., Vorobiev Y.V. (2010). *Nanocrystals and quantum dots of group IV semiconductors*. American Scientific Publishers.
- Remes Z., Novak T., Stuchlik J., Dřinec V., Fajgar R., Zhuravlev K. (2014): Infrared photoluminescence spectra of PbS nanoparticles prepared by Langmuir–Blodgett and laser ablation methods. *Acta Polytechnica*, 54(6), 426–429. doi:10.14311/AP.2014.54.0426
- Galkin N.G., Galkin K.N., Chernev I.M., Fajgar R., Stuchlikova T.H., Stuchlik J., Remes Z. (2015): Formation and properties of p–i–n diodes based on hydrogenated amorphous silicon with embedded CrSi, MgSi and CaSi nanocrystallites for energy conversion applications. *JJAP Conference Proceedings*, 3, 11104. doi:10.7567/JJAPCP.3.011104
- Stuchlikova T.H., Fajgar R., Kostejn M., Drinec V., Remes Z., Stuchlik J. (2015): The laser ablation as a perspective technique for the deposition of metal-silicide nanoparticles in situ embedded in PECVD of Si:H thin films. *JJAP Conference Proceedings*, 3, 11302. doi:10.7567/JJAPCP.3.011302
- Stuchlik J., Stuchlikova T.H., Remes Z., Purkrt A., Fajgar R., Koštejn M., Zhuravlev J.K., Kupčík A., Sveshnikova L., Galkin K.N., Galkin N. G. (2015): The Combined Technological Methods for Deposition of Si:H Thin Films and Structures with Embedded NPs. *Advanced Science, Engineering and Medicine*, 7(4), 265–269. doi:10.1166/asem.2015.1689
- Galkin K.N., Galkin N.G., Dózsa L., Dotsenko S. A., Chernev I. M., Vavanova S. V., Dobos L., Pécz B. (2013): Growth, structure, optical and electrical properties of Si/2D Mg₂ Si/Si(111) double heterostructures and Schottky diodes on their base: Growth, structure, optical and electrical properties of Si/2D Mg₂ Si/Si(111) double heterostructures and Schottky diodes on their base. *Physica Status Solidi*, 10, 1720–1723. doi:10.1002/pssc.201300366
- Stuchlik J., Stuchlikova T.H., Artemenko A., Remeš Z. (2015): Deposition of magnesium silicide nanoparticles by the combination of vacuum evaporation and hydrogen plasma treatment. *JJAP Conference Proceedings*, 3, 11301. doi:10.7567/JJAPCP.3.011301
- Chernev I.M., Shevlyagin A.V., Galkin K.N., Stuchlik J., Remes Z., Fajgar R., Galkin N.G. (2016): On the way to enhance the optical absorption of a-Si in NIR by embedding Mg₂Si thin film. *Applied Physics Letters*, 109(4), 43902. doi:10.1063/1.4960011
- Fojtik A., Valenta J., Stuchlikova T., Stuchlik J., Pelant I., Kočka J. (2006): Electroluminescence of silicon nanocrystals in p–i–n diode structures. *Thin Solid Films*, 515(2), 775–777. doi:10.1016/j.tsf.2005.12.190

11. Daldosso N., Pavesi L. (2009): Nanosilicon photonics. photonics. *Laser & Photonics Reviews*, 3(6), 508–534. doi:10.1002/lpor.200810045
 12. Valenta J., Greben M., Remeš Z., Gutsch S., Hiller D., Zacharias M. (2016): Determination of absorption cross-section of Si nanocrystals by two independent methods based on either absorption or luminescence. *Applied Physics Letters*, 108(2), 23102. doi:10.1063/1.4939699
 13. Jackson W.B., Amer N.M., Boccara A.C., Fournier D. (1981): Photothermal deflection spectroscopy and detection. *Applied optics*, 20(8), 1333–1344. doi:10.1364/AO.20.001333
 14. Vaněček M., Poruba A., Remeš Z., Beck N., Nesládek M. (1998): Optical properties of microcrystalline materials. *Journal of Non-Crystalline Solids*, 227, 967–972. doi:10.1016/S0022-3093(98)00202-6
 15. Ledinský M., Vetushka A., Stuchlík J., Mates T., Fejfar A., Kočka J., Štěpánek J. (2008): Crystallinity of the mixed phase silicon thin films by Raman spectroscopy. *Journal of Non-Crystalline Solids*, 354(19), 2253–2257. doi:10.1016/j.jnoncrysol.2007.09.073
-