

GERMANIUM AND TIN NANOPARTICLES ENCAPSULATED IN AMORPHOUS SILICON MATRIX FOR OPTOELECTRONIC APPLICATIONS

The Ha STUCHLIKOVA, Zdenek REMES, Jiri STUCHLIK

Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic, EU hotheha@fzu.cz, remes@fzu.cz, stuj@fzu.cz

Abstract

The plasma enhanced chemical vapour deposition was combined with in situ deposition of Ge and Sn thin film by evaporation technique at surface temperature about 220 °C to form nanoparticles on the surface of hydrogenated silicon thin films to prepare diodes. Formation of nanoparticles was additionally stimulated by plasma treatment through a low pressure hydrogen glow discharge. The diodes based on PIN diode structures with and without the embedded Ge or Sn nanoparticles were characterized by temperature dependence of electrical conductivity, activation energy of conductivity, measurement of volt-ampere characteristics in dark and under solar illumination.

Keywords: a-Si:H, Ge NPs, Sn NPs, diode structures, I-V characteristics

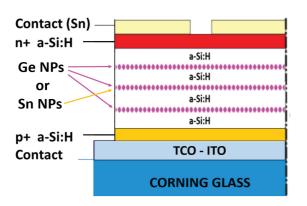
1. INTRODUCTION

The efficiency and stability improvement of inexpensive solar cells based on amorphous hydrogenated silicon (a-Si:H) were very attractive are actual up to now. The question how to increase too weak photo- and electro-luminescence of amorphous hydrogenated silicon is open too. Our effort is focused on a possibility to deposit *in situ* amorphous or microcrystalline Si:H thin films with embedded nanoparticles (NPs). We choose the semiconductors which band gap is below the band gap of a-Si:H. For it we develop new deposition systems, which allow combine convenient deposition techniques. In this contribution we pay attention to germanium, but in the contrary with lot of published attempts to apply a-Si_xGe_y:H alloys in the photovoltaic [1,2], even the a-Si_xSn_y:H alloys were studied [3], we prefer form of Ge nanoparticles (Ge NPs) integrated into intrinsic a-Si:H structure. Special attention we paid to behaviour of tin. Ge NPs and tin nanoparticles (Sn NPs) were encapsulated in a-Si:H thin films to improve optoelectronic properties of this thin layer structures. Presented work has continuity on previous published results [4 - 8].

2. EXPERIMENTAL

The intrinsic a-Si:H film was deposited by plasma enhanced chemical vapour deposition (PECVD) technique on a fused silica glass substrates size 10x5 mm at surface deposition temperature 220 °C. During interruption of PECVD the vacuum chamber was pumped up to 10⁻⁵ Pa and on the a-Si:H surface the germanium or tin films were evaporated in the thickness of 1 nm. The elements formed isolated NPs on the a-Si:H surface with support of hydrogen plasma treatment. Then the deposited NPs were covered and stabilized by a-Si:H layer by PECVD. Both deposition processes were alternated 5 times. Finally on the surface were evaporated two titanium strips with the distance 2 mm. By this way were deposited samples with Ge NPs - 3K93 and samples with embedded Sn NPs - 3K78, 3K79 and 3K80. Those alloys with integrated Ge or Sn NPs with the co-planar configuration of electrodes were characterized by measurement of temperature dependence of electrical conductivity. On the Corning glasses covered by transparent conductive layer (ITO) after previous deposition of p-type of a-Si:H. were deposited a-Si:H films which were immediately in situ covered by Ge or Sn nanoparticles. The NPs were formed on a-Si:H surface during Vacuum Evaporation (VE) of Ge thin film with thickness 1 nm and Sn thin films with thicknesses 1 or 0.3 nm. By this way were deposited final PIN diode structures 3K95 with Ge NPs and 3K90 and 3K91 with embedded Sn NPs - see **Figure 1**.





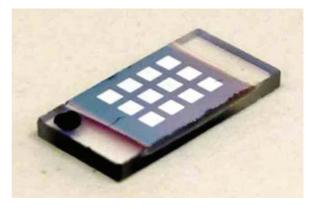


Figure 1 Schematic illustration of PIN diode structures with embedded NPs and photography of the size 10x5 mm sample with 12 diodes. Ge NPs were embedded in the intrinsic layer in 1/4, 1/2 and 3/4 of its thickness, the Sn NPs only in the 1/2 of its thickness.

3. RESULTS AND DISCUSSION

For characterization of semiconductors the temperature dependence of electrical conductivity i.e. Arrhenius plot is important measurement, see **Figure 2**. While the integration of Ge NPs increases the conductivity and decreases the activation energy of conductivity only little, the effect of Sn NPs is marked in changes of activation energy. The relatively light increases of conductivities at the room temperature 293 K for samples with Sn NPs proved the NPs are well mutually insulated by a-Si:H thin film.

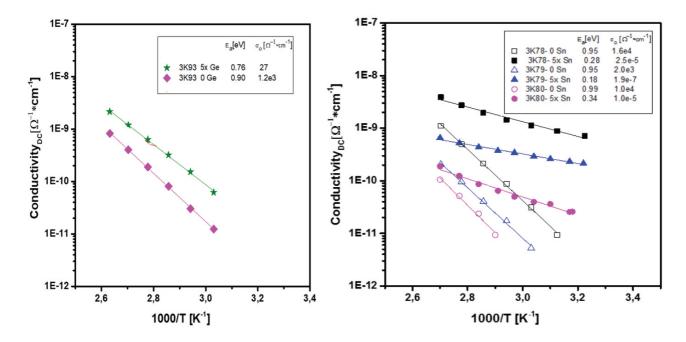


Figure 2 Temperature measurement of electrical conductivity (Arrhenius plot) of reference samples and samples with 5 times integrated monolayers of Ge (left picture) and Sn NPs (right picture)

In the case of measurement of I-V characteristics we compare two diode structures with and without Ge or Sn NPs. Here the deposition and creation of Ge NPs was repeated 3 times for one diode and at same time for second diode the deposition process of a-Si:H was interrupted only. The measurement of I-V characteristics in dark gives the first results, both currents (reverse and forward) increased, see **Figure 3**.



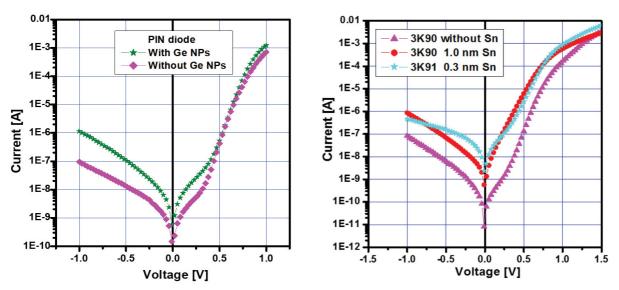


Figure 3 I-V characteristics of PIN diode measured in dark with 3 evaporated Ge monolayers of thickness 1.0 nm. Monolayers of formed Ge NPs are in the middle and at 1/4 and 3/4 of intrinsic a-Si:H thin film (3K95 - left picture), one monolayer of Sn NPs is only in the middle of a-Si:H (3K90 and 3K91 - right picture).

Most important is the measurement under illumination by solar simulator. From the results shown on the **Figure 4**. we conclude the Voltage open current ($V_{oc} = 0.67 - 0.68 \text{ V}$) is same for both PIN diodes and as well as the Fill Factor (FF = 64) does not change too.

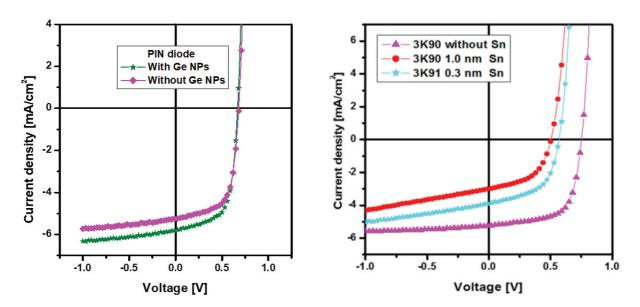


Figure 4 I-V characteristics of PIN diodes (3K95) measured under illumination by solar simulator. Requested effect of Ge NPs on the characteristic parameters of PV elements is demonstrated by increase of I_{sc} while V_{oc} and FF are without changes (see left picture) and as well as measurement of PIN diodes (3K90 and 3K91 - right picture) with embedded Sn NPs with different sizes.

Positive effect of Ge NPs we observe on short circle Current (Isc increases from 52 to 58 μ A), for small photovoltaic element size 0.64 mm². On the contrary the integration of Sn NPs if the evaporated thickness was same i.e. 1 nm the effect on the basic parameters of diodes was negative while the smaller size of Sn NPs (evaporated thickness 0.3 eV) leads toward an increase of those characteristics values.



4. CONCLUSION

In this contribution we demonstrate possibility to integrate Ge or Sn NPs to intrinsic layer of PIN diodes on the base of a-Si:H thin films. Although the measurements in dark of I-V characteristics of the diode structures show negative effect on the reverse current the increase of forward current is positive. The most important result which we introduce here is the increase of I_{sc} if the Germanium is in the form of NPs embedded in diode structures while the U_{oc} and FF remain same. The integration of Ge NPs leads toward the requested increase efficiency of very thin film PV elements which are only a few tenths of nm. In the case of metallic Sn NPs we demonstrate surprising result - although the influence on diode parameters is negative, the character of diodes were preserved. The negative impact of NPs increases with the increase of NPs size.

ACKNOWLEDGEMENTS

This work was supported by the CSF project 16-10429J, the MEYS project LTC17029 INTER-COST Action MP1406 and by the Operational Programme Research, Development and Education financed by European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports (Project No. SOLID21 - CZ.02.1.01/0.0/0.0/16 019/0000760).

REFERENCES

- [1] HAMAKAWA. Y. *Amorphous semiconductor technologies and devices silicon*. Japan Annual Reviews in Electronics Computers and Telecommunications, Vol.6, Tokyo: OHMSHA, LTD, 1983, p. 135
- [2] FRITZSCHE. H. *Amorphous silicon and related materials*, Advances in Disordered Semiconductors Vol. 1, Singapore: Word Scientific Publishing Co. Pte. Ltd., Vol 1B, 1989, p.887
- [3] HAMAKAWA. Y. *Amorphous semiconductor technologies and devices silicon*. Japan Annual Reviews in Electronics Computers and Telecommunications, Vol.22, Tokyo: OHMSHA, LTD, 1987, p. 99
- [4] KRIVYAKIN, G. K., VOLODIN, V. A., SHKLYAEV, A. A., MORTET, V., MORE-CHEVALIER, J., ASHCHEULOV, P., REMES, Z., STUCHLIKOVÁ, T. H., STUCHLIK, J., Formation and study of p-i-n structures based on two-phase hydrogenated silicon with a germanium layer in the i-type region, *Semiconductors 51* 2017, pp 1370 1376.
- [5] CHERNEV, I. M., SHEVLYAGIN, A. V., GALKIN, K. N., STUCHLÍK, J., REMEŠ, Z., FAJGAR, GALKIN, N. G. On the way to enhance the optical absorption of a-Si in NIR by embedding Mg2Si thin film, *Appl. Phys. Lett.* 109, 2016, pp. 043902-1 - 043902-4.
- [6] KRIVYAKIN, G. K., VOLODIN, V. A., KOCHUBEI, S. A., KAMAEV, G. N., PURKRT, A, REMEŠ, Z., FAJGAR, R., STUCHLIKOVÁ, T. H., STUCHLIK, J., Optical properties of p-i-n structures based on amorphous hydrogenated silicon with silicon nanocrystals formed via nanosecond laser annealing, *Semiconductors* 50, 2016, pp. 935 940.
- [7] DVURECHENSKII, A.V., VOLODIN, V.A., KRIVYAKIN, G.K., SHKLYAEV, A.A., KOCHUBEI, S.A., NEIZVESTNY, I.G., STUCHLIK, J., Raman Studies of Phase and Atomic Compositions of GeSi Nanosystems after Pulsed Annealing, *Optoelectronics, Instrumentation and Data Processing 52*, 2016, pp. 496-500.
- [8] STUCHLÍKOVA, T. H., FAJGAR, R., KOŠTEJN, M., DŘÍNEK, V., REMEŠ, Z., PURKRT, A., STUCHLÍK, J., 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 Conf. Proc.* 3, 2015, pp. 011302-1 011302-5.