

Amorphous hydrogenated silicon /a-Si:H/ thin films deposited by PE-CVD and used as light emitting diode structure containing Titan Dioxide /TiO₂/ nanoparticles

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ABSTRACT

N-type, p-type and intrinsic a-Si:H thin films were deposited on glass, ITO/glass and Si substrates by using RF-PECVD system with the following conditions: $P_{\text{working}} = 1$ torr, $T_{\text{substrate}} = 400\text{K}$, RF power density was of $150\text{mW}/\text{cm}^2$ and the H_2/SiH_4 ratio was of 5/1. A band gap of the deposited film was determined from the transmittance and reflectance spectra that were measured in a wavelength range from 300 nm to 1800 nm. The band gap was found to be of ca. 2 eV. Raman spectra and IR spectra of the films indicate that the deposited films were formed in amorphous with hydrogen concentration 13, 7 % which have been suitable for applications. The hybrid PIN diode structures were made in which a hybrid layer was composed of TiO₂ nanoparticles (prepared by pulsed laser ablation) embedded in intrinsic a-Si:H thin film. The investigation of the Photoluminescence of diode structures and aqueous TiO₂ solutions showed that a red-shift in maximum PL peak of TiO₂. The unstable visible light emission which could be observed by naked eyes from diodes showed that this hybrid diode structure can be used for electroluminescence device.

INTRODUCTION

A typical amorphous hydrogenated silicon (a-Si:H) solar cell is a PIN device applied widely on the world by its high optical absorption coefficient and very low manufacturing cost. Recently, a combination between a-Si:H with nanoparticles having a large band gap or conducting polymers create hybrid structures that can be created electroluminescence devices, advanced photocatalysis or high efficiency solar cell...[3, 5]. In this report, we document the “home made” PE-CVD. Intrinsic, n-type and p-type a-Si:H thin films and PIN diode structures were deposited on different substrates (coming 7059 glass, ITO/glass, Si...) from Silane (SiH₄) as principal precursor and hydrogen as carrier gas. By this system we investigate a new kind of light emitting junction based on a-Si:H.

EXPERIMENTAL

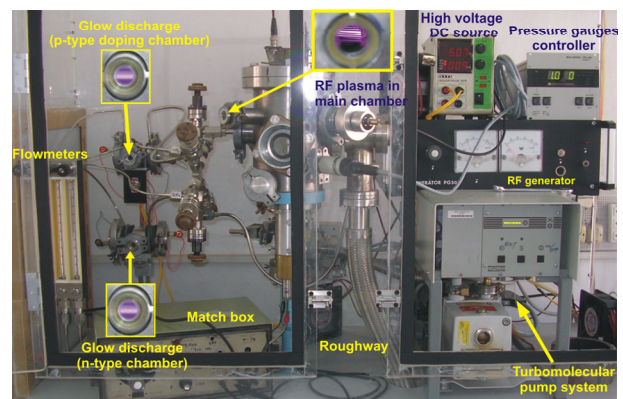


Figure 1: The “home-made” PE-CVD system.

PE-CVD system (figure 1) were rebuilt from some non-used old vacuum systems in our

laboratory (at Solid State Physics Department – University of Natural Sciences, Vietnam).

The main chamber can be evacuated to the pressure value 10^{-6} Torr. RF plasma was used for deposition with the frequency 13.56 MHz. N-type and P-type doping was performed by solid source (P or B powder in hydrogen DC glow-discharges from small separated chambers).

The deposition conditions of above a-Si:H thin films are: The ratio between SiH_4 and H_2 flow-rate is 1:5 and substrate temperature is 400K. The RF power density is $150\text{mW}/\text{cm}^2$ and DC glow-discharge current density for doping is $1\text{mA}/\text{cm}^2$. At the working pressure of 1 Torr, the growth rate of film is approximately $1.4\text{Angstrom}/\text{s}$.

Optical and electronic properties and structure characteristics of as-deposited Si:H thin films were investigated by FTIR spectra, Raman spectra (Bruker Equinox spectrometer), and UV-Vis spectra (Jasco 530 spectrometer) in University of Natural Sciences, HCMC - Vietnam.

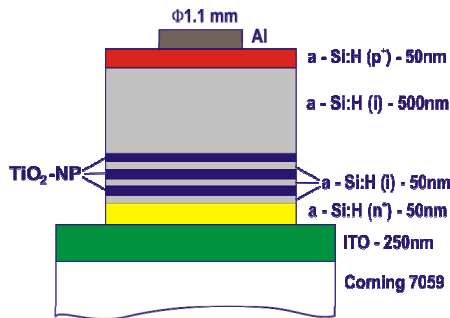


Figure 2: Schematic cross-section of $\text{TiO}_2\text{-NP}/\text{a-Si:H}$ diodes.

The hybrid PIN diode is described in figure 2 in which the mixture between an intrinsic a-Si:H with TiO_2 nanoparticles plays a role of emitting layer. The used TiO_2 nanoparticle was prepared from TiO_2 or Ti target in deionized water by laser pulsed ablation method [4]. Similarly, the PIN diode structures without TiO_2 nanoparticles were also prepared for comparing the effects of TiO_2 nanoparticles.

Photoluminescence and electroluminescence of aqueous TiO_2 nanoparticle solution and diodes were investigated by P-L and E-L measuring equipments in Faculty of Nuclear Sciences and Physical Engineering CTU, Institute of Physics of the ASCR in Prague and University of Natural Sciences, HCMC - Vietnam.

RESULTS AND DISCUSSIONS

Optical properties and structure characteristic of single thin films

The NIR-VIS transmission and reflection spectra of intrinsic Si:H thin films on corning glass and ITO/glass and Si substrates with the same deposition conditions are shown in figure 3. The optical band gap estimated from transmission spectra is about 2eV, which is the typical value for amorphous Si:H [3]. The multiple fringes are due to interference effects.

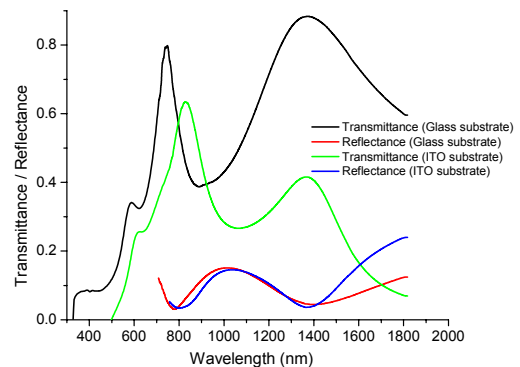


Figure 3: Transmission and reflection spectra of Si:H films on Corning and ITO substrates.

The Raman spectrum of above a-Si:H thin film with deposition time 120 minutes and thickness $1\mu\text{m}$ (figure 4) having a broad peak at 484cm^{-1} indicates also that the structure of films is amorphous [3].

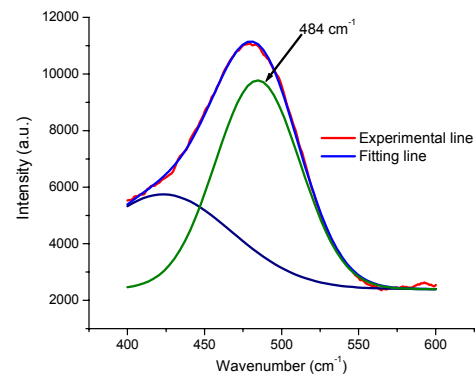


Figure 4: A Raman spectrum of sample with deposition time is 120 minutes.

Figure 5 shows the IR absorption peak at about 650cm^{-1} of films on Si substrates, which are the characteristic vibrations of Si-H group [1, 2]. The

empirical spectra were fitted with Lorentz function. Hydrogen concentrations calculated using the method described in [1, 6] are 13.7% atom and 13.3% atom for the samples with deposition time 60 minutes and 120 minutes, respectively.

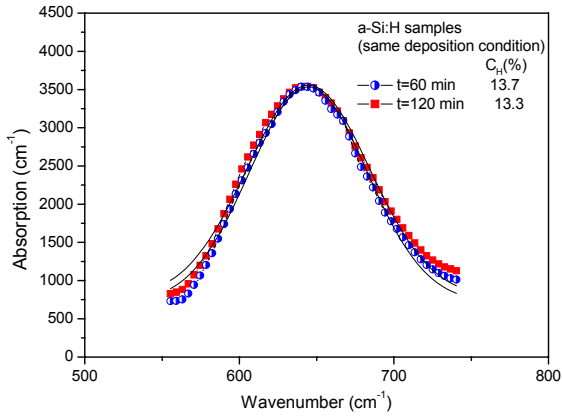


Figure 5: Absorption peak of samples with different deposition time.

I-V, P-L and E-L characteristics of diodes

Photoluminescence (P.L) spectra of TiO₂ nanoparticles with excitation wavelength 250 nm (figure 5) indicate some different features between the particles produced from different target. However, the two spectra both have peaks at about 380nm (3.27eV), which are close to the optical band gap of TiO₂ bulk material.

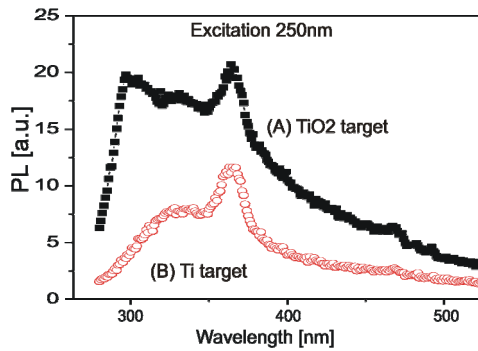


Figure 5: Photoluminescence spectra of TiO₂ NP.

In figure 6, the microscopy photographs of diode structure are shown. In structures without TiO₂-NP, a featureless smooth surface of diodes is observed. On the contrary, inhomogeneous and rough structures appear in TiO₂-NP contained diodes, demonstrating clearly the mixing of nanoparticles and Si:H layer.

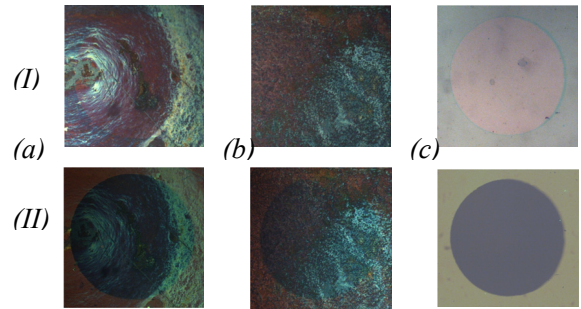
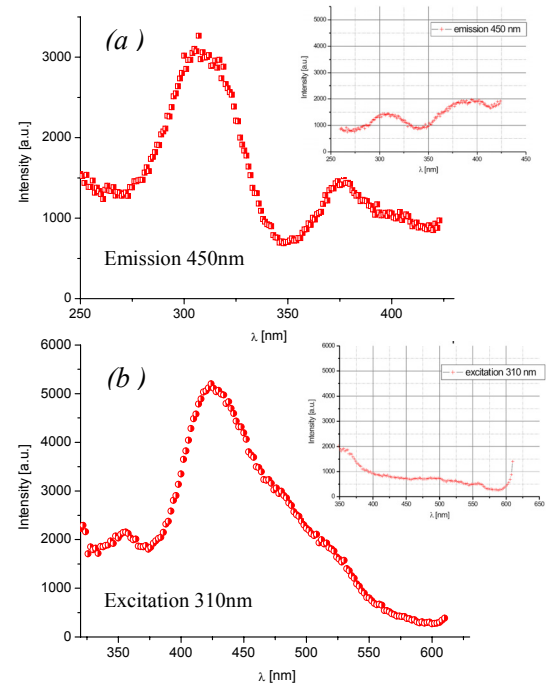


Figure 6: Microscopy photographs of diode structures illuminated by white light. (I): illuminating from ITO side; (II): illuminating from both side of the diodes. (a): diode with NP from TiO₂ target; (b): diode with NP from Ti target and (c): without NP.

Excitation P.L. and P.L spectra of the diode structures containing TiO₂-NP compared with those without nanoparticles are shown figure 7. The excitation P.L spectra of diode structure have maximum peaks at 310nm (4eV) whereas the P.L spectra of them having maximum peaks at 425nm (2.9eV), which are smaller in energy than the maximum peak (3.27 eV) in P.L. spectra of TiO₂ nanoparticles above. The observed red-shift phenomena [7] may be due to the mixture between a wide band gap semiconductor (TiO₂) in matrix of a narrow band gap one (a-Si:H).



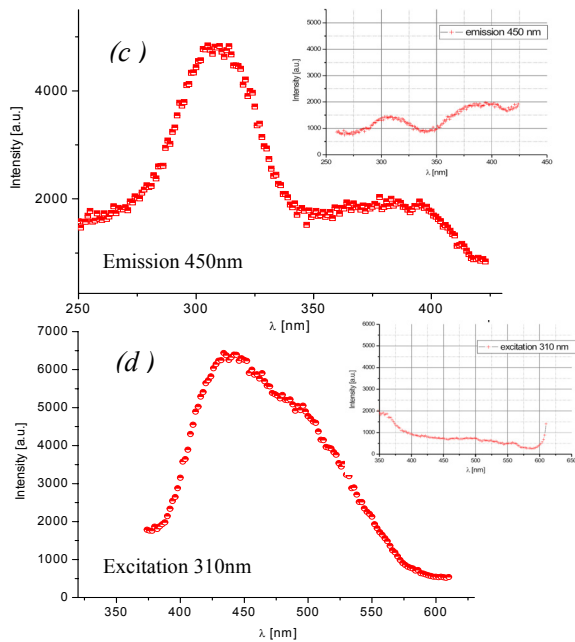


Figure 7: Excitation P.L. (emission at 450nm) and P.L. (excitation at 310nm) spectra of diode structures with NP prepared from TiO₂ (a, b) and Ti (c, d) target. The insets in (a) (c) and (b) (d) are the corresponding excitation P.L. and P.L. spectra of the structure without NP.

Figure 8 represents the I-V characteristics and electroluminescence photographs of diode structure containing the two kinds of TiO₂-NP. Open voltages of diodes are 2 V and 5 V depending on kind of TiO₂ NP. When the voltage is about 9 – 10 V, there are unstable light emissions which could be observed by naked eyes from diodes.

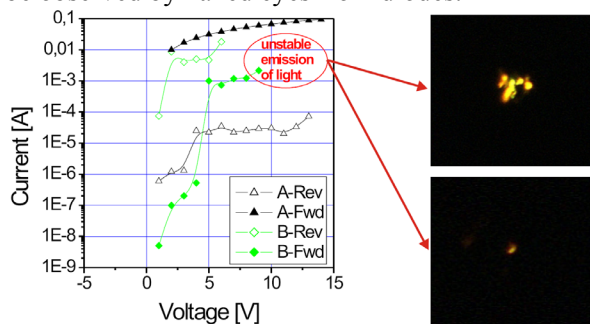


Figure 8: I-V characteristics and photographs of light emitting from diode structures.

CONCLUSIONS

In this report, we have rebuilt a stable-working PECVD for deposition of intrinsic, n-type and p-

type a-Si:H in our laboratory at Vietnam. The optical and structural analysis shows that the achieved thin films were composed of hydrogen content 13,7 at% H₂. The deposited intrinsic a-Si:H thin film was mixing with a different kind of TiO₂ nanoparticles made from laser pulsed ablation method in order to create some hybrid PIN diode structures. The comparison between photoluminescence spectra of those diodes with spectra of an aqueous TiO₂ NP solution indicates a red-shift in maximum peak. I-V characteristics and microscope photographs illustrate a light emitted ability of the diode structures.

ACKNOWLEDGEMENT

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