

**Ellipsometric investigation of laser textured silicon  
surfaces and pulsed laser deposited amorphous silicon and  
 $\text{Si}_x\text{C}$  thin films**

PhD dissertation theses

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# 1 Introduction

Silicon is undoubtedly today's most important technological material. In addition to the electrical properties of silicon and silicon-based materials, their optical properties are becoming increasingly important, because of the demands of both the photovoltaic technology and new emerging technologies combining electronic circuits with optical circuits. Developing applications continue to provide broad opportunities for scientific research, therefore I deal with production and investigation of silicon-based materials in my thesis. During my work I used laser-based material production techniques, which have been intensively studied and successfully applied in the recent history of the Department of Optics and Quantum Electronics at University of Szeged. In this work the spectroscopic ellipsometry was the main sample characterization technique. This method allows fast measurement without damaging the sample, and it provides the optical properties of the sample and the thicknesses of the potential layers by means of a modeling procedure. My research was focusing both on the ellipsometric investigation of the samples prepared by different laser processing methods and on the critical interpretation of the ellipsometric results.

## 2 Literature and aims

The silicon surface structuring is often used to increase the efficiency of detectors or solar cells made of silicon. Multiple laser pulse irradiation is a clean and non-contact method for this purpose. Typical applied laser intensities for texturing Si surfaces are lower than those which can initiate material removal for a single shot of irradiation. The effect of the first laser pulses determine how the process will proceed. However, the initial changes in case of very small intensities can be so minor that they are invisible for microscopic techniques. *Therefore, my aim was to structure silicon surfaces with low intensity nanosecond and subpicosecond laser pulses and to follow the processes using spectroscopic ellipsometry.*

When the silicon surface is irradiated with sufficiently high intensity pulses, then material removal occurs and silicon thin film can be made. This is the principle of pulsed laser deposition. Amorphous silicon thin films are used for example in solar cells. However, its structure is not stable because of dangling bonds, therefore these dangling bonds need to be passivated by incorporating hydrogen. *My aims were to produce hydrogenated amorphous silicon films onto silicon and glass substrates by pulsed laser deposition, and to investigate how the optical properties and also the composition of the films change as a function of hydrogen pressure.*

Silicon-carbon composite thin films can be made by combining silicon and carbon materials. An important feature of such layers is that the optical properties (e.g. band gap) can be tuned by varying the composition. Although the silicon-carbon thin films are usually prepared by plasma enhanced chemical vapor deposition, pulsed laser deposition can be suitable technique as well. *Therefore, my goal was to create  $\text{Si}_x\text{C}$  thin films with different compositions by pulsed layer deposition of compound targets containing silicon and carbon parts of different sizes. My aim was to investigate the connection between the target configuration and the composition of the final thin film. A further object was to investigate, how the optical properties, density and bonding structure of the thin films change with the composition.*

I used oscillator models in the ellipsometric characterization of the silicon-carbon thin films. Oscillator parameters are often used to indicate tendencies in the changes of the optical properties of the material. However, the optical properties are determined by the composition and structure of the material. Therefore, the oscillator parameters are in connection with the microscopic properties of the sample. Hence, the parameter changes can be good indicators also for microscopic properties if the meaning and sensitivity of the parameters are clarified. Since the microscopic properties of the silicon-carbon sample series vary in a wide range, *my goal was to compare the Tauc–Lorentz and*

*Gauss models in the ellipsometric characterization of the silicon-carbon samples, and to investigate both the sensitivity of the parameters and the dependencies of the model parameters on the composition.*

### **3 Methods**

Silicon surfaces were textured by subpicosecond and nanosecond duration laser pulses, generated by a hybrid dye-KrF excimer laser and a KrF excimer laser, respectively. Amorphous silicon and silicon-carbon thin films were prepared by pulsed laser deposition. ArF excimer laser was used for these experiments. The amorphous silicon films were deposited in hydrogen atmosphere with different hydrogen pressures. The silicon-carbon thin films were created by ablating two-component targets containing pure silicon and carbon parts.

The optical properties and thickness of the laser textured silicon surface layers and the pulsed laser deposited films were determined by spectroscopic ellipsometry. A Woollam M2000F and a Semilab GES5E devices were used. The surface of the amorphous silicon films were investigated with a Nikon Optiphot 100 S optical microscope and a PSIA XE100 atomic force microscope. The surface structures of the laser textured silicon samples were investigated with a Hitachi S-4700 scanning electron microscope at Faculty of Science and Informatics, University of Szeged, while the Raman spectra of the surfaces were recorded with a Thermo DXR Raman microscope at Department of Mineralogy, Geochemistry and Petrology, University of Szeged. The compositions of the amorphous silicon and silicon-carbon thin films were determined by backscattering spectrometry and elastic recoil detection. The measurements were carried out in the Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences. The bonding structure of the silicon-carbon films was investigated with X-ray photoelectron spectroscopy. The

measurements were made in the Department of Physical Chemistry and Materials Science, University of Szeged.

## **4 New scientific results**

**I.** The changes of crystalline silicon samples irradiated with subpicosecond and nanosecond KrF laser pulses having intensity below the ablation threshold were investigated. It was pointed out based on the ellipsometric and Raman spectroscopic results, that in case of the subpicosecond laser the first laser pulse causes the formation of a  $\sim 15$  nm thick amorphous silicon layer and as a resulting effect of the subsequent pulses the layer becomes thicker and has higher mechanical stress. In case of the illumination with nanosecond laser pulses it was established, that the surface changes in  $\sim 250$  nm depth, but its structure remains almost completely crystalline. Based on the distortion of the optical properties of the modified layer and the shifts of the Raman spectra it was concluded, that mechanical stress occurs during the re-solidification, which can originate in the defects of the crystallization. With increasing pulse number the structure of the layer is increasingly different from that of the substrate due to the cumulating crystal defects, and it can be detected by ellipsometry and Raman spectroscopy. Based on temperature distribution calculations it was established, that the material re-solidifies with 100 ps and 140 ns after the pulses in case of the subpicosecond and nanosecond pulses, respectively. The three order of magnitude difference explains the observed differences in the bonding structure of the modified layers. Based on the electronmicroscopic images and the decreasing of the ellipsometric fitting quality it was pointed out, that the surface becomes structured after 5 and 100 pulses, in case of the subpicosecond and nanosecond pulses, respectively. [S1]

**II.** Amorphous silicon films were prepared by pulsed laser deposition with ArF excimer laser onto silicon and glass substrates in hydrogen atmosphere. The

properties of the films were investigated as a function of hydrogen pressure. Based on the results of the ellipsometry, backscattering spectrometry and elastic recoil detection it was pointed out, that with increasing hydrogen pressure not only hydrogen but oxygen incorporates into the films as well, which causes a decrease in absorption and refractive index. Besides, the surface of the films becomes rougher. It was established, that the films have depth gradient both in optical properties and oxygen concentration: the lower refractive index at the bottom of the films is caused by the lower oxygen concentration. A linear connection was found between the optical properties gradient and oxygen concentration gradient. [S2]

**III.** Amorphous silicon-carbon films with different compositions were prepared by pulsed laser deposition with ArF excimer laser alternately ablating the two parts of a combined target consisting of pure silicon and pure carbon parts of different sizes. It was established, that films with arbitrary composition can be prepared by changing the size – in fact the total ablation time – of the two target parts. It was pointed out based on the backscattering spectrometric results of the films deposited from pure silicon and pure carbon, that carbon has  $\sim 3.6$  times higher deposition rate than silicon. Using this result a calibration line was established, which can be used to determine the appropriate target part size ratios in order to reach a planned  $x$ : Si/C ratio. [S3]

**IV.** The optical properties, density and bonding structure of the films created by pulsed laser deposition using ArF laser were investigated as a function of  $x$ : Si/C ratio. Based on the results of ellipsometry, backscattering spectrometry, elastic recoil detection and X-ray photoelectron spectroscopy it was pointed out, that the macroscopic and microscopic properties of the films change continuously with the variation of Si/C ratio. Based on the results four typical composition range were distinguished:

- Diamond like carbon film was deposited from the pure carbon target. The film has high density, high refractive index, wide band gap, small absorption, its optical functions are similar to those of diamond, and it consists of mostly  $sp^3$ -hybridized carbon atoms.
- The diamond like character turns to graphite like in case of small silicon content. These films have smaller density than the diamond like carbon film, their band gap is zero or close to zero, they have higher absorption at small photon energies and they have anomalous refractive index dispersion. The graphitization of the films was explained by the effect of the high energy silicon ions in the plasma.
- Around  $x = 1$  Si/C ratio silicon-carbide like films were deposited. The density of the films falls between that of the diamond like carbon film and the graphite like films, the band gap is wide. The Si-C bonds are dominant in the bonding structure besides C-C bonds.
- By the highest silicon content amorphous silicon film was grown. This film has the smallest density, wide band gap, high absorption above 2 eV, high refractive index, and it contains mostly Si-Si bonds. [S3]

V. The Tauc–Lorentz and Gauss models accompanied with Sellmeier model were compared in the ellipsometric evaluation of silicon-carbon films with different composition. It was established that both models are capable of characterizing the optical properties of the  $Si_xC$  films, but in case of  $x > 1$  the Tauc–Lorentz model performed better. This was explained by the difference in the high energy behavior of the oscillators.

It was established by the mathematical analysis of the models, that the model parameters and the actual parameters of the  $\varepsilon_2$  function (position of the maximum, full width at half maximum – FWHM, area under the curve) are linearly connected if certain conditions are met. It was pointed out that the oscillator positions are good estimates of the  $\varepsilon_2$  maximum position if the

oscillator broadenings are small compared to the oscillator positions, and if the band gap is around 1/3 of the oscillator position in case of the Tauc–Lorentz model. It was established that in case of small broadening the parameter is a good approximate of the FWHM of  $\varepsilon_2$ , while in case of higher values overestimates it. It was pointed out based on the results, that the oscillator position and broadening parameters are good estimates of the  $\varepsilon_2$  maximum position and its FWHM in the composition range of  $x < \sim 0,04$  and  $x > \sim 1$ . However, in the composition range of  $\sim 0,04 < x < \sim 1$  the position parameter of Gauss model underestimates, while that of Tauc–Lorentz model overestimates the maximum position of  $\varepsilon_2$ , and both broadening parameters overestimate its FWHM.

It was established that the total absorption of the oscillators (area under the  $\varepsilon_2$  curve) are mainly determined by the amplitude parameter, especially with increasing broadening. Accordingly, the total absorption of the  $\text{Si}_x\text{C}$  films in the investigated photon energy range is well-characterized by both of the amplitude parameters.

By investigating the sensitivity of the parameters it was established, that the uncertainty of the oscillator parameters increases in case of high broadening values. It was pointed out, that the reason of the parameter insensitivity is that the maxima of the oscillators are out of the investigated photon energy range in these cases.

The oscillator parameters were correlated to the various types of chemical bonding present in the samples. It was established, that the amplitude, broadening and band gap values depend mainly upon the Si  $\sigma$ - $\sigma^*$  and C  $\pi$ - $\pi^*$  electronic transitions, whilst the amplitude parameter of the Sellmeier model is coupled to the  $\sigma$ - $\sigma^*$  transitions of C–C bonds or of Si–C bonds. [S4]

## 5 Publications

### Referred publications supporting the thesis points



[S1] Z. Toth, **I. Hanyecz**, A. Gárdián, J. Budai, J. Csontos, Z. Pápa, M. Füle: Ellipsometric analysis of silicon surfaces textured by ns and sub-ps KrF laser pulses, Thin Solid Films, accepted for publication

[S2] **I. Hanyecz**, J. Budai, E. Szilagyi, Z. Toth: Characterization of pulsed laser deposited hydrogenated amorphous silicon films by spectroscopic ellipsometry, Thin Solid Films 519 (9) (2011) 2855-2858  
Number of independent citations: 3

[S3] **I. Hanyecz**, J. Budai, A. Oszko, E. Szilagyi, Z. Toth: Room temperature pulsed laser deposition of  $\text{Si}_x\text{C}$  thin films in different compositions, Applied Physics A 100(4) (2010) 1115-1121  
Number of independent citations: 4

[S4] J. Budai, **I. Hanyecz**, E. Szilagyi, Z. Toth: Ellipsometric study of  $\text{Si}_x\text{C}$  films: Analysis of Tauc-Lorentz and Gaussian oscillator models, Thin Solid Films 519 (9) (2011) 2985-2988  
Number of independent citations: 1

### Further referred publications

[5] M. Bereznai, J. Budai, **I. Hanyecz**, J. Kopniczky, M. Veres, M. Koós, Z. Toth: Ellipsometric study of nanostructured carbon films deposited by pulsed laser deposition, Thin Solid Films 519 (9) (2011) 2989-2993

[6] T. Csizmadia, B. Hopp, T. Smausz, J. Kopniczky, **I. Hanyecz**, Á. Sipos, M. Csete, G. Szabó: Possible application of laser-induced backside dry etching technique for fabrication of SERS substrate surfaces, Applied Surface Science 278 (2013) 234-240

[7] T. Csizmadia, B. Hopp, T. Smausz, Z. Bengery, J. Kopniczky, **I. Hanyecz**, G. Szabó: Fabrication of SERS active surface on polyimide sample by excimer laser irradiation, Advances in Materials Science and Engineering (2014) art. no. 987286

[8] Z. Pápa, J. Budai, **I. Hanyecz**, J. Csontos, Z. Toth: Depolarization correction method for ellipsometric measurements of large grain zinc-oxide films, Thin Solid Films, accepted for publication