

Femtosecond and Nanosecond Laser Pulse Crystallization of Thin a-Si:H Films on Non-Refractory Glass Substrates

V.A.Volodin^{1,2, a}, M.D.Efremov^{1, b}, G.A.Kachurin¹, S.A.Kochubei¹,
A.G.Chervov¹, M.Deutschmann³, and N. Baersch³

¹Institute of Semiconductor Physics SB RAS, Lavrentjeva ave., 13, Novosibirsk 630090, Russia,

²Novosibirsk State University, Pirogova street 2, Novosibirsk 630090, Russia

³Laser Zentrum Hannover, Hollerithallee 8, 30419 Hannover, Germany

^aE-mail of contacting author: volodin@isp.nsc.ru

^bE-mail of presenting author: efremov@isp.nsc.ru

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Abstract. Thin (90 nm) a-Si:H films on Corning 7059 glass substrates have been crystallized by 120 fs pulses of Ti:sapphire and nanosecond pulse XeCl and KrF excimer lasers. Initial films were deposited using low-temperature plasma enhanced deposition technique. The structural properties of the films were characterized using the spectroscopy of Raman scattering, excited by the argon laser (line 514.5 nm) and using electron microscopy. For the femtosecond pulse treatments the ablation threshold was found to be some more than 65 mJ/cm². When pulse energy density was lower than ~30 mJ/cm² no structural changes were observed. In optimal regimes the films were found to be fully crystallized with needle grain structure, according to the Raman scattering and electron microscopy data. Estimates show the pulse energy density was lower than the Si melting threshold, so non-thermal "explosive" impacts may play some role. The main result in nanosecond XeCl and KrF laser pulse crystallization is the narrower window between beginning of crystallization and ablation for KrF laser (wavelength 248 nm) than for the XeCl laser (wavelength 308 nm). So, the possibility of the femtosecond and nanosecond laser pulses to crystallize a-Si films on non refractory glass substrates was shown. The results obtained are of great importance for manufacturing of polycrystalline silicon layers on non-refractory large-scale substrates for giant microelectronics.

Introduction

The interest in amorphous silicon films on non-refractory substrates and their crystallization is constantly stimulated by demands of giant microelectronics. For example, the enlargement of sizes of flat panel displays with active thin film transistor matrix can be described as "reverse Moore's law" [1]. Modern technique of deposition allows producing of a-Si films on substrates with plasticity temperature as low as 100 °C. For some applications the poly-silicon films have many advantages comparing with a-Si films. So, the development of low thermal budget technology of crystallization of a-Si films is actual, and is of interest up today, especially for femtosecond laser crystallization [2, 3].

Experimental

Sample preparation and treatments. The initial thin (90 nm) a-Si:H films were deposited on Corning 7059 glass substrates (temperature of plasticity 593 °C) using low-temperature (230 °C) plasma enhanced deposition technique. According to IR-spectroscopy and light transmission data, the films contain up to 20 atomic % of hydrogen. For laser pulse crystallization the excimer XeCl

and KrF lasers and Ti:sapphire laser were used. The parameters of XeCl laser: wavelength $\lambda=308$ nm, pulse duration 25 ns. The parameters of KrF laser: wavelength $\lambda=248$ nm, pulse duration 20 ns. The laser spot in the case of nanosecond excimer laser treatments had rectangular shape with sizes of several millimeters. The 120 fs Ti:sapphire laser pulses with wavelength of 800 nm, pulse energy 0.8 mJ, and repetition rate of 1 kHz were used. In this case, the laser irradiation was focused to round spot with 280 micron in diameter, the spot was scanned, using x-y sample translation by computer-controlled motors.

Methods for structural analysis. The structural properties of the films were characterized by the Raman scattering spectroscopy, excited by the argon laser (line 514.5 nm). Quasi-backscattering geometry was used with falling light angle being equal to Brewster angle. The incident light was linearly polarised, polarization of scattered light was not analysed. The study of structure of the films was also carried out using high-resolution electron microscope JEOL-4000EX.

Results and discussion

In the case of nanosecond laser pulse crystallization the treatments below and higher than the a-Si melting and ablation thresholds were applied. The result of laser treatments on structure of the films is shown in fig. 1.

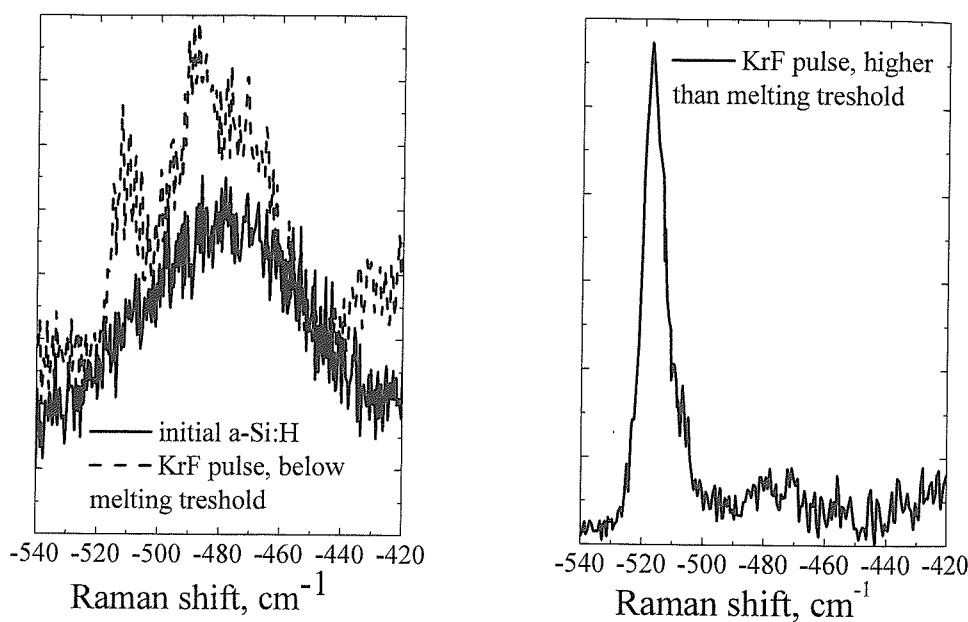


Fig. 1. Raman spectra of initial a-Si film and films treated by KrF laser with energy density lower (left) and higher (right) than melting threshold.

When the energy density of KrF laser pulse was 100 mJ/cm^2 or lower no structural changes were observed in Raman spectra (1 shot was used). The spectrum in figure 1 (dashed line) is for sample treated by KrF laser pulse with energy density 130 mJ/cm^2 . One can see in this spectrum not only "amorphous" peak (broad, $\sim 480 \text{ cm}^{-1}$) but also "nanocrystalline" peak ($\sim 510 \text{ cm}^{-1}$). The Raman spectrum of a-Si is the broad peak at approximately 480 cm^{-1} appearing as result of effective density of vibration modes [4]. Due to scattering on optical phonon modes localised in the nanocrystals, the

Raman spectrum of nanocrystals. The position and the width of according to dispersion of the dispersion of the nanocrystals. nanocrystal phase; so, one can $V_{\text{nano-Si}} = I_c / (I_c + \sigma_a I_a)$

where σ_a is relation between the data, σ_a can change from 0.1 for the volume fraction of nanocrystal density 130 mJ/cm^2 is about 0.1

In figure 1 (right) the Raman than melting threshold is shown almost all film was crystallized suppose that crystallites have energy in pulse was 200 mJ/cm^2

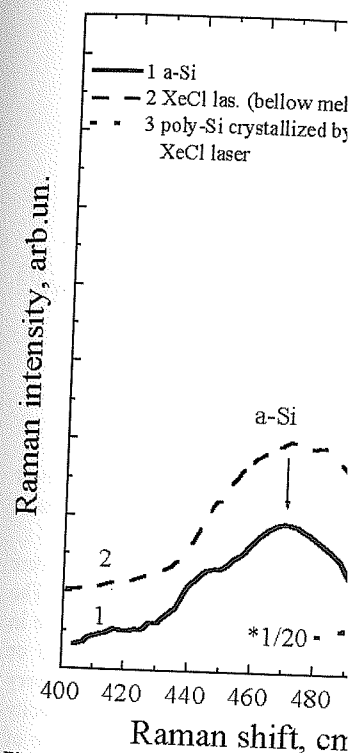


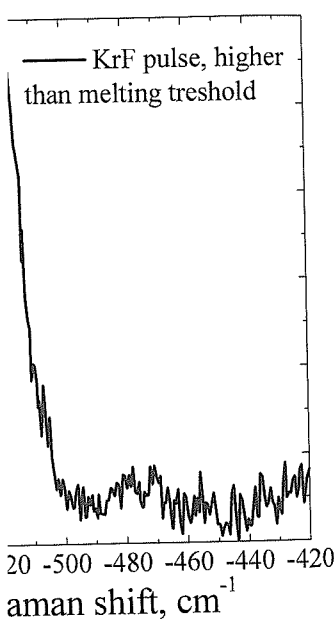
Fig. 1. Raman spectra of initial a-Si film and films treated by XeCl laser with energy density lower (100 mJ/cm^2) and higher (260 mJ/cm^2) than melting threshold.

As one can see from figure 2, the energy density about 100 mJ/cm^2 or higher. So, it was on the threshold of crystallization and of ablation threshold may be due to higher absorption coefficient

XeCl laser: wavelength $\lambda=308$ nm, pulse duration 20 ns, pulse energy 10 mJ. The samples had rectangular shape with dimensions 10 mm x 10 mm. The wavelength of 800 nm, pulse duration 10 ns. The laser irradiation was focused on the sample using x-y sample translation by

the films were characterized by Raman spectroscopy (wavelength 514.5 nm). Quasi-backscattering geometry was used. The incident light was at normal incidence. The study of structure of the films was done by JEOL-4000EX.

samples below and higher than the melting threshold. The effect of laser treatments on structure of the



laser with energy density lower (left)

lower no structural changes were observed. Figure 1 (dashed line) is for sample treated by XeCl laser with energy density lower than melting threshold. One can see in this spectrum not only the amorphous peak (~460 cm⁻¹) but also a small crystalline peak (~510 cm⁻¹). The Raman intensity is decreasing as a result of effective density of states localized in the nanocrystals, the

Raman spectrum of nanocrystals is characterised by narrow peak at position between 500-520 cm⁻¹. The position and the width of the peak strongly depend on size and structure of the nanocrystals according to dispersion of the localised modes [5]. The peak width is mainly determined by size dispersion of the nanocrystals. The intensity of the "nanocrystal" peak depends on the contents of nanocrystal phase; so, one can determine the volume part of nanocrystal phase:

$$V_{\text{nano-Si}} = I_c / (I_c + \sigma_a I_a) \quad (1),$$

where σ_a is relation between the integral cross sections of crystal Si and a-Si. According to literature data, σ_a can change from 0.1 for large grain polycrystalline silicon up to 0.88 for nano-Si [6]. So, the volume fraction of nanocrystalline phase in sample treated by KrF laser pulse with energy density 130 mJ/cm² is about 0.1.

In figure 1 (right) the Raman spectrum of sample treated by KrF laser with energy density higher than melting threshold is shown. The energy density in this case was 170 mJ/cm². One can see that almost all film was crystallized. The position of crystalline peak is close to 520 cm⁻¹, so, one can suppose that crystallites have good structure quality and relatively big sizes. When the density energy in pulse was 200 mJ/cm² and higher, the full ablation of the films took place.

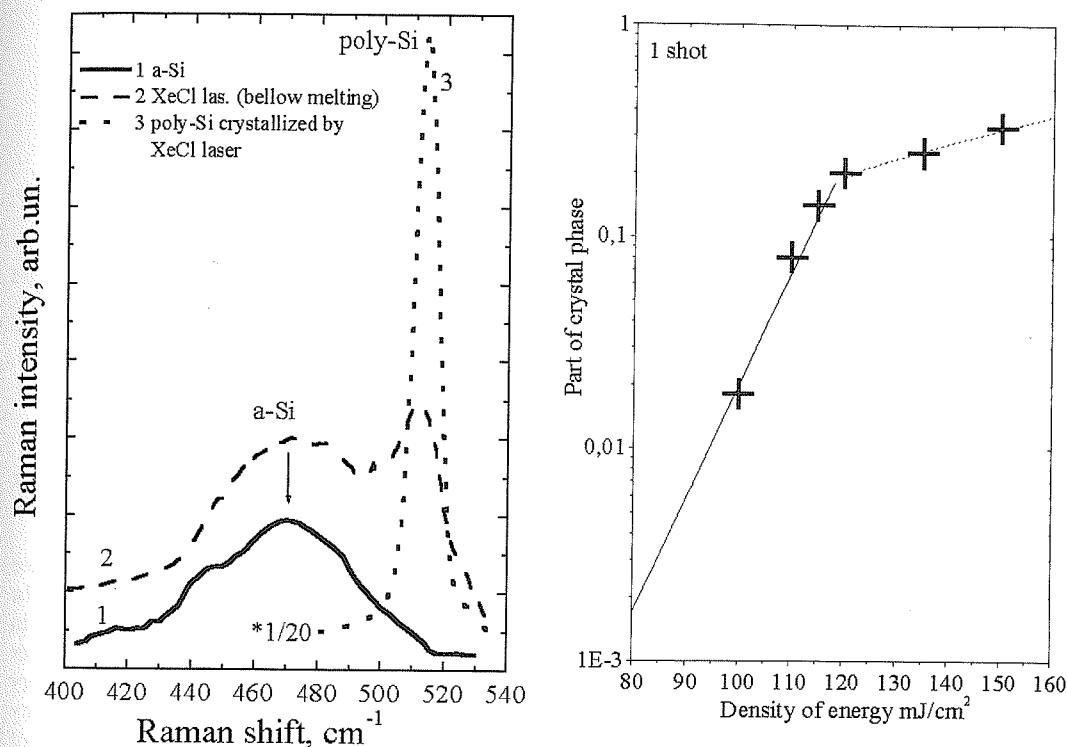


Fig. 1. Raman spectra of initial a-Si film and films treated by XeCl laser with energy density lower (110 mJ/cm²) and higher (260 mJ/cm²) than melting threshold (left). The part of crystalline part versus density of energy in XeCl laser pulse (right).

As one can see from figure 2, the beginning of crystallization for XeCl treatments took place for energy density about 100 mJ/cm². The beginning of ablation took place when energy density was 280 mJ/cm² or higher. So, it was obtained, that "window" in energy density between beginning of crystallization and of ablation threshold is narrower for KrF laser comparing with the XeCl one. It may be due to higher absorption coefficient of light with wavelength of 248 nm.

In the case of femtosecond laser pulse treatments the ablation threshold was found to be of about 65 mJ/cm^2 . When pulse energy density was lower than $\sim 30 \text{ mJ/cm}^2$ no structural changes were observed. In optimal regimes the films were found to be fully crystallized with fine grain structure, according to the Raman scattering data (fig. 3).

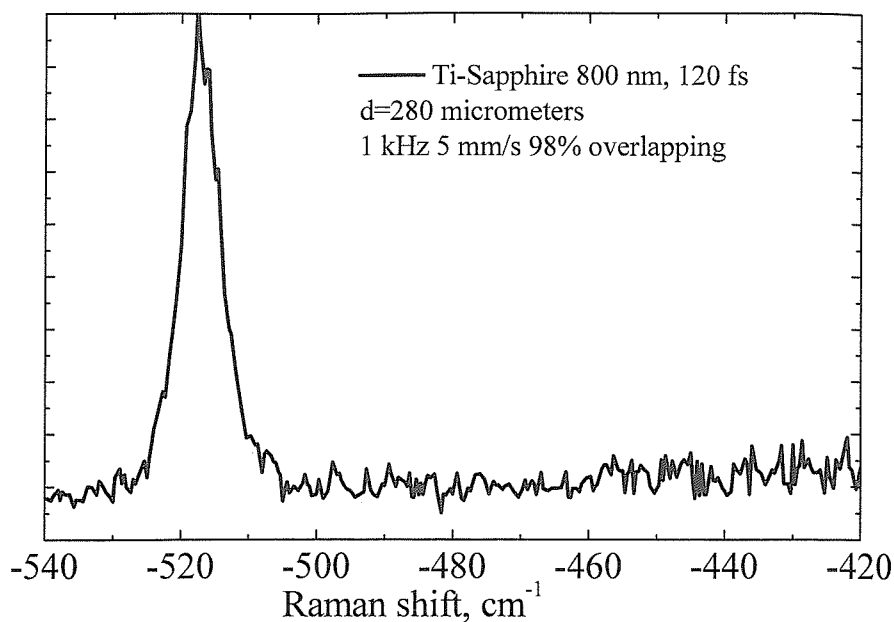


Fig. 3. Raman spectrum of Si film fully crystallized by femtosecond laser pulse treatment.

The energy density in this case (fig. 3) was 65 mJ/cm^2 . When pulse energy density was lower than $\sim 30 \text{ mJ/cm}^2$ no structural changes in the films were observed in Raman spectra, when pulse energy density was 100 mJ/cm^2 the films were fully ablated.

To investigate, what part of energy in pulse was absorbed by the films, the next experiments were carried out. The reflectance and transmittance of the light in spectral region were measured. The results are presented in figure 4. As one can see, for not intensive, probe beam, the absorbance in the film at 800 nm is low. Only $7 \pm 3\%$ of energy is absorbed, and main part is reflected or transmitted. So, for the energy density 65 mJ/cm^2 the films absorb less than 5 mJ/cm^2 . For very short time of pulse, the absorbed energy can not dissipate in substrate, so, knowing the heat capacity of 90 nm Si film, one can easy calculate what temperature of film will be during absorbance of energy. This result is presented in figure 5. If assume the thermal mechanism of crystallization, at temperature about 600°C (absorbed energy density 5 mJ/cm^2), the time of crystallization should be tens of hours. But the 120 fs is not enough for thermalization of hot electrons and holes generated by absorbed phonons. The time of thermalization about $1\text{--}2 \text{ ps}$ [7]. So, electron temperature is higher than phonon temperature in the case of power femtosecond pulses. Also not-linear effects can lead to enlargement of absorbance in this case – two-photon effects, absorbance in not-linear power electric field and additional absorbance in optical transitions in hot electron-hole plasma.

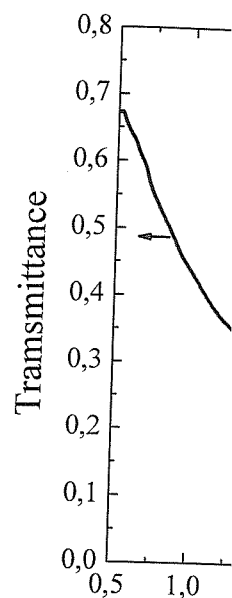


Fig. 4. Reflectance and transmiss

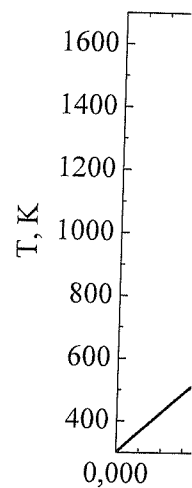
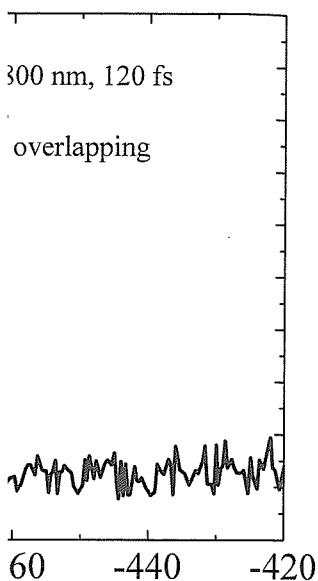


Fig. 5. Calculated temperature of f

threshold was found to be of about 10^4 J/cm² no structural changes were observed with fine grain structure,



and laser pulse treatment.

The pulse energy density was lower than in Raman spectra, when pulse

films, the next experiments were carried out in the central region were measured. The probe beam, the absorbance in the central region, and main part is reflected or absorbed less than 5 mJ/cm². For very short pulses, so, knowing the heat capacity of the film will be during absorbance of the laser pulse. The mechanism of crystallization, at the time of crystallization should be determined by the number of electrons and holes generated [7]. So, electron temperature is determined by the laser pulses. Also not-linear effects in the absorbance in not-linear in hot electron-hole plasma.

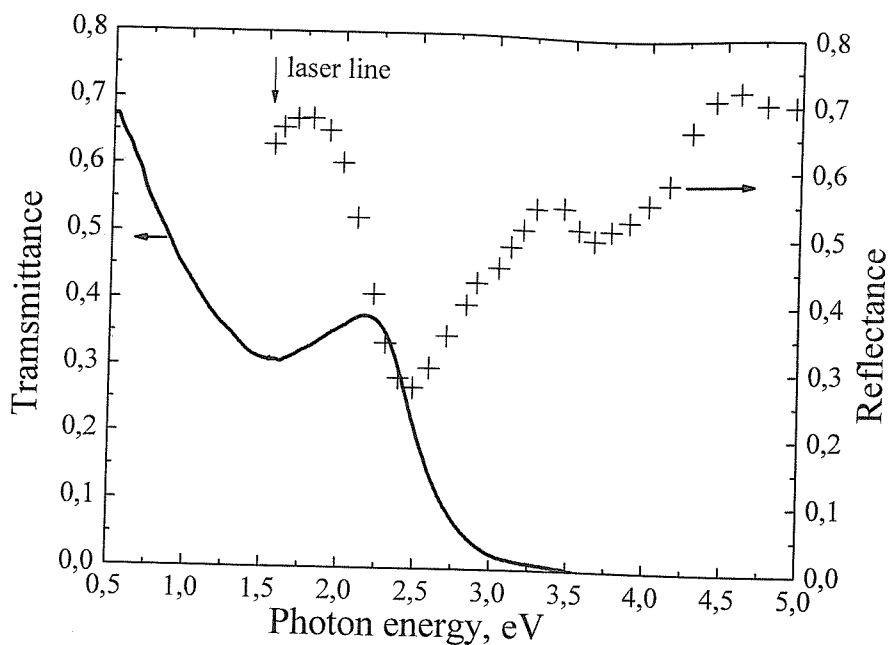


Fig. 4. Reflectance and transmission spectra of initial a-Si:H film.

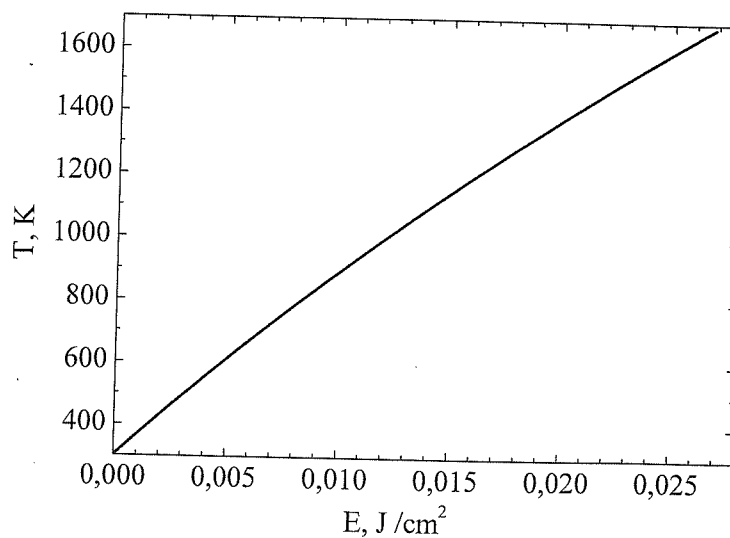


Fig. 5. Calculated temperature of film versus absorbed energy.

The complex refraction coefficient for plasma is:

$$N = \sqrt{\epsilon_0 - \frac{\omega_p^2}{\omega^2 + \frac{i\omega}{\tau}}}, \text{ where } \omega_p^2 = \frac{4\pi e^2 n}{m_{\text{eff}}} \quad e - \text{elementary charge, } n - \text{free electron}$$

concentration, m_{eff} – effective mass. So, for $n = 10^{20}$ – 10^{21} cm^{-3} the absorbance can 2-5 times higher, than for a-Si:H films without hot plasma.

It is known, that silicon appears unstable when concentration of electron-hole pairs is higher than 10^{21} cm^{-3} [7]. To reach such concentration, the 90 nm Si films should absorb 22 mJ/cm^2 (the photon energy is 1.55 eV). It is lower than energy needed for thermal mechanism crystallization – 53 mJ/cm^2 (this energy needed for heating and melting of this film). The relative absorbance in this case should reach $53/65=0.82$ what is unlikely even taking into account the non-linear effects in absorbance. So, the numerical estimates show the pulse energy density was lower than the Si melting threshold, so non-thermal “explosive” impacts may play some role.

Summary

It was obtained, that “window” in energy density between beginning of crystallization and of ablation threshold is narrower for KrF laser comparing with the XeCl one.

The possibility of the femtosecond laser pulses to crystallize Si films on glass substrates was shown. Non-linear effects and non-thermal “explosive” impacts may play some role in femtosecond treatments. The results obtained are of great importance for manufacturing of polysilicon layers on non-refractory substrates for thin film microelectronics.

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DLTS and PR spectroscopy

Ł. Gelczuk^{1, a}

¹Faculty of Microelectronics

^alukasz.gelczuk@pwr.edu.pl

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Abstract. The study of partially-strain relaxed phase epitaxy (MOVPE) and photorefraction trap has been attributed to the EL2 point defect. By applying the results of DLTS measurements were able to estimate the concentration of relaxed epitaxial layer.

Introduction

The electrical and optical properties of substrates are strongly affected by heterostructures for optical devices. It can be pseudomorphic growth of a material with lattice mismatch is accommodated (depending on the sign of the mismatch) between heavy and light bands [1]. After exceeding a certain critical thickness, dislocations at the interface of the structure. Both kinds of defects are the form of closely spaced traps for free carriers and acceptor levels.

In this paper, we present the results of In_xGa_{1-x}As/GaAs heterostructure deep-level transient spectroscopy (DLTS) techniques. The DLTS measurements show the presence of at least two deep levels in the presence of misfit dislocations. The DLTS-line behaviour, point defects and dislocations, as well as the effect of residual strain on the conduction and valence band splitting.