Aluminum diffusion during laser-stimulated crystallization of thin silicon films

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Abstract. Diffusion of aluminum in amorphous silicon films during crystallization through infrared laser irradiation was studied. Diffusion regime was found to change from limited source to abundant source diffusion at higher laser source power. At the same time, crystalline structure of the obtained samples becomes more perfect, which is more characteristic to limited source diffusion mode.

1. Introduction
Here we report results of investigations on aluminum diffusion in thin silicon films upon irradiation with infrared laser at varied regimes. Laser stimulated diffusion found application in preparation of semiconductor materials with pn junction. For this, the substrate surface is covered with a thin layer of doping agent followed by pulsed laser beam irradiation [1]. Upon diffusion of atoms from the doping layer, a pn junction is formed near the surface of the substrate. This technology can be utilized for preparation of a wide variety of semiconductor devices, including highly effective solar energy panels [2] for sustainable energy harvesting.

Thin silicon films were crystallized following previously described protocols [3,4]. The method relies on absorbing metal coating deposited onto the surface of amorphous silicon which is then irradiated with pulsed 1064 nm laser. Silicon and most of the substrates, including glass and polymers, do not absorb in this range, in contrast to metals (particularly, aluminum). Thus, it is only the top metal coating that is directly heated by laser irradiation. Generated heat is then dissipated to the silicon film, which results in recrystallization of the latter. High localization of the process allows for low melting (decomposition/glass transition) temperature materials to be utilized as substrates, which undergoes almost no heating shock. This opens perspective for preparation of semiconductor devices upon various types of substrates, such as flexible polymeric ones.

Due to the mechanism of heat dissipation in the structure, a strong temperature gradient presents in the silicon film between its surfaces (metal-silicon and silicon-substrate planes), which provides circumstances for diffusion of metal atoms into silicon. Absorbing metal layer in this system can be considered as a dopant source. Thus, aluminum diffusion in silicon films at varied parameters of laser irradiation was studied in this work.
2. Materials and methods

For absorption of laser irradiation, 300 nm thick aluminum coatings were deposited onto 1 µm thick silicon film. Both coatings were prepared by magnetron sputtering with Angstrom NexDep machine (Angstrom Engineering, Canada) using argon as working gas. The machine is equipped with two magnetron sources with 3” targets, which allowed for the process to be performed in a single vacuum cycle. Glass 25x75 mm 1 mm thick microscope slides were utilized as substrates.

Prepared samples were irradiated in ambient air in normal lab conditions with 1064 nm pulsed laser using a Minimarker 2 machine (Laser Center, Russia) equipped with a computer-controlled scanning head which can create patterns on samples up to 50x50 mm. In this work, 10x10 mm squares were irradiated. Laser power was varied between samples (0.2, 0.4 and 0.6 W) with all other parameters remaining constant. Laser scanning velocity was 200 mm/s, pulse duration was 100 ns, pulses repetition rate was 99 kHz, objective-sample distance 115 cm. The laser spot diameter was 25 µm, so with irradiation parameters mentioned above each point on the sample surface was irradiated with more than 10 laser pulses. At each power level, four similar samples were prepared for substantial analysis and repeatability studies of crystalline structure.

Silicon phase state in annealed films was characterized by means of Raman spectroscopy, calibrated using single-crystalline silicon. Map spectroscopy measurements were performed with InVia (Renishaw, UK) microscope (532 nm laser, up to 0.01 mW incident power, 50x lens). All measurements were performed in mapping mode allowing to understand the correlation of optical sample look and spectral data.

Secondary-ion mass-spectrometry (SIMS) depth profiles were registered with Perkin-Elmer PHI 4300 setup equipped with a quadrupole mass-analyzer. Sputtering was carried out with Ar+ primary ions with energy 4 keV.

3. Results and discussion

Reflected white light microscopic images of the irradiated samples surface (made in course of Raman spectroscopy measurements) are presented in Fig. 1. At higher laser irradiation powers the surface of the samples becomes less homogeneous with dark areas which seem to be large silicon crystallites.

![Figure 1. Reflected white light microscopic images of irradiated samples. A – sample irradiated with laser power 0.2 W; B – 0.4 W; C – 0.6 W. The scalebar corresponds to 10 µm](image)

Aluminum content depth profiles measured by means of SIMS are presented in Fig. 2, where all data sets are normalized to 1. Two types of aluminum profiles can be distinguished. At lower irradiating laser power levels of 0.2 and 0.4 W aluminum content smoothly decreases with depth, which is characteristic for diffusion from abundant source [5]. In contrast, for samples prepared at higher laser power (0.6 W) aluminum profile peaks at certain depth with the maximum concentration of aluminum in the film. Such behavior can be attributed for diffusion process happening from a limited source [5].
Figure 2. Aluminum depth profiles for laser irradiated samples obtained by SIMS

Raman studies demonstrated presence of 520 cm$^{-1}$ c-Si peak in all samples regardless the irradiating laser power. For analysis and comparison, peak was fitted by Voigt function to obtained data after smoothing and background subtraction, and then fitted peak position and full width at half maximum (FWHM) were averaged between all measurements points for similar samples, and standard deviation was calculated. Obtained data are presented in Figure 3.

Figure 3. Fitted crystalline silicon peak parameters from Raman measurements
SIMS measurements results demonstrate switch of dopant diffusion source type from abundant to limited at particular irradiating laser power. We can attribute this change to the way aluminum is ablated from the silicon surface. At lower laser power (0.2 and 0.4 W) simultaneous ablation of aluminum and its diffusion into silicon happen. After the laser pulse, some residue of aluminum film remains. Thus, the dopant source (aluminum coating) does not exhaust during single laser pulse, i.e. remains abundant. At higher power (0.6 W) both ablation and diffusion happen more rapidly, so aluminum is fully evaporated and diffused to the depth of silicon film, which renders dopant source limited, which is confirmed by characteristic SIMS profile data for such samples.

From Raman data, silicon is recrystallized in all samples. However, c-Si peak FWHM standard deviation is very high (>1.82 cm\(^{-1}\)) for samples prepared at lower laser powers (0.2, 0.4 W), which evidences poor homogeneity of resulting crystalline structure, which is further confirmed by rather broad cSi peaks (FWHM > 7.5 cm\(^{-1}\)). Oppositely, FWHM values become significantly less (together with standard deviations of those) in samples prepared at laser power of 0.6 W (6.25±0.73 cm\(^{-1}\)), which corresponds to most perfect crystalline structure among all the obtained samples [6].

4. Conclusion
If put together, SIMS and Raman studies results propose correlation of diffusion mechanism of doping atoms from absorbing layer and the crystalline structure of resulting silicon films after laser ablation. Diffusion of aluminum atoms during laser irradiation promotes crystallization of amorphous silicon, while the intensity of the process improves the perfection of resulting film crystalline structure. This is in agreement with a known effect of layers interchange during aluminum induced crystallization (AIC) [7].

Obtained results open perspectives for polycrystalline silicon films preparation with controlled doping profiles upon isolating, semiconductive and conductive substrates. Synthesis of materials with controlled (e.g., gradient) properties variation (particularly, conductivity) in the depth, also seems perspective for designing ultrathin electromagnetic waves absorbers, including metamaterials-inspired ones [8].

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