Thin amorphous silicon films crystallization upon flexible substrates

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Abstract. A novel method for thin silicon films crystallization that combines advantages of laser- and metal-induced crystallization technologies is reported. Polycrystalline silicon films were synthesized on flexible polyimide substrates following the proposed approach. Films obtained possess high crystal structure regularity and crystallinity.

1. Introduction
In modern field of microelectronics, designing devices on flexible substrates is of high interest. One of main technological problems here is preparation of polycrystalline silicon films upon such substrates [1]. Polymeric films, which otherwise are a good and straightforward choice for the purpose, cannot be treated at high temperatures (as high as 1000 °C) that are necessary for conventional silicon crystallization. Various methods are proposed recently to overcome this limitation aiming for low temperature processing. Among most widely applied approaches are laser-induced (LIC) [2] and metal-induced (MILC) [3] crystallization. In LIC, cost reduction by use of simpler and cheaper laser irradiation sources (of near infrared range) is a challenge [4]. Use of near-IR laser is restricted by low absorption of silicon in this range.

Here we present experiments on crystallization of amorphous silicon films upon flexible polyimide substrates deposited by DC magnetron sputtering. For this, recently published original technique that combines abovementioned approaches (LIC and MILC) for low temperature crystallization is applied [5]. Deposition of absorbing metal layers on top of amorphous silicon film allows for use of near-infrared laser for crystallization. Furthermore, metal layer also serves as crystallization promoter similar to the way it happens in MILC process.

2. Materials and Methods
All films were deposited on the surface of 0.5 mm thick polyimide substrates that were cleaned following standard RCA Standard Clean procedure using Nexdep vacuum magnetron sputtering system (Angstrom Engineering Inc., Canada) with oil-free vacuum pumping system. Planar magnetron ONYX 3 (Angstrom Science, USA) was utilized with disc silicon cathode (99.999% clean, diameter of 76.2 mm, Girmet, Russia) and EQ1R1200 (Glassman High Voltage, USA) power supply in DC mode.
A set of 4 samples (see table 1) was prepared differing by presence of additional buffer [6] and absorbing layers. Buffer layer of SiO\textsubscript{x} (thickness of 1 µm) was deposited immediately on polyimide film prior to silicon sputtering (samples C and D). Then, 1 µm silicon film was deposited. These layers were deposited in a single process without intermediate chamber venting. Substrate temperature was kept at 150 °C during buffer and silicon layers deposition, metal layer was deposited at room temperature. As a last step, 200-300 nm thick nickel or aluminum laser absorption layer was formed on top of silicon film for samples B,C,D.

Resulting structures were annealed with 1064 nm pulsed YAG:Nd fiber laser in 10x10 mm squares (achieved by scanning of laser beam focused in ~25x25 µm spot with Gaussian power distribution). Single pulse fluence is equal to 2.038 J cm\textsuperscript{-2} (except sample A). With pulse duration of 100 ns, its average power density was ~20 M W cm\textsuperscript{-2}. For sample A, which had no metal absorption coating, laser power density was elevated 5 fold to achieve crystallization. Metal film served both as laser radiation absorption layer and crystallization inducer [5]. Upon laser irradiation, metal coating was heating and ablated, transferring some portion of heat to underlying amorphous silicon film. As a result, silicon crystallization to polycrystalline state was achieved in a regime that polyimide substrate could tolerate.

For each sample structure, several experiment repetitions were performed, and averaged characteristic data are reported.

| Sample | SiO\textsubscript{x} buffer layer | a-Si layer | Absorption layer |
|--------|-----------------------------------|------------|-----------------|
| A      | –                                 | +          | –               |
| B      | –                                 | +          | Ni              |
| C      | +                                 | +          | Ni              |
| D      | +                                 | +          | Al              |

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.

Optical imaging was performed using IX-73 inverted microscope (Olympus, Japan) in transmitted white light using 10x lens.

3. Results and discussion
Optical images of the samples obtained are presented in figure 1. As imaging is performed in transmitted light, bright areas are transparent and colored yellow by polyimide film. Please note, that exposure is varied throughout the presented images, thus absolute brightness levels cannot be compared. Despite the elevated laser power used for annealing, darker non-crystalline areas are visible in figure 1A. Furthermore, silicon film is severely exfoliated, probably due to high local heat-induced stresses. This renders impossible use of near-IR laser for direct crystallization of amorphous silicon films.
Figure 1. Optical images in transmitted white light of laser-irradiated samples. Positions lettering corresponds to samples labeling.

Together with great annealing laser power reduction, absorbing metal layer deposited on top of silicon films significantly induces homogeneity of crystallized film (figure 1B). However, pronounced cracking of silicon film is evident, which can be attributed to different thermal expansion coefficients of silicon and polyimide, as well as flexibility of the substrate.

Introduction of buffer layer between polyimide substrate and amorphous silicon film allows for obtaining a whole crystallized silicon films with almost no cracks and exfoliations (figure 1C). Dark areas if figure 1C,D correspond to traces of metal layer which are not fully removed. With the thickness of buffer layer equal to that of silicon film, temperature field gradient is significantly reduced on the substrate-film interface. Therefore, differences of thermal expansion coefficients of substrate and silicon film are leveled by increase of heat transfer pathway [6].

When aluminum is utilized for absorbing layer, the surface of the resulting silicon film is also intact (figure 1D). Thus, aluminum films can also be used as absorbing layer in the combined method utilized [5].

From Raman spectra (figure 2A) of all samples investigated, a peak at 520 cm$^{-1}$ is present, in very rare cases accompanied by a lower broader peak of amorphous silicon near 480 cm$^{-1}$, which evidences successful silicon crystalline phase formation during laser ablation process. However, based on results of optical images analysis, it can be concluded that buffer and absorbing layers are necessary for whole film of crystalline silicon formation. Due to presence of exfoliations and cracks in samples A and B and areas of amorphous silicon in sample A, crystalline peak was only found in particular areas of annealed film surface for these samples. For samples C and D, however, relatively high crystalline silicon peak was found everywhere throughout the surface except the absorbing layer metal residuals, which cloak the silicon surface from observations. Figure 2B,C present optical images obtained from Raman microscope (reflected light, metal residuals appear brighter) during mapped spectral acquisition with green overlaid circles at individual measurements points. For samples C (figure 2B) and D (figure 2C), crystalline peaks usually appear at all points (with obvious variation in peak height due to masking by metal) despite the differences in morphology of these.
Average full width at half maximum (FWHM) of crystalline silicon peak at 520 cm\(^{-1}\) for sample C was 5.2\(\pm\)0.9 cm\(^{-1}\). For single-crystal silicon wafer used for calibration, this value is about 4.0 cm\(^{-1}\), thus it can be concluded that annealed films attain high crystalline structure regularity with estimated crystalline phase portion as high as 88\% [7].

Figure 2. Raman spectra acquisition of crystallized silicon films. A - Characteristic Raman spectra for all samples, vertical line is at 520 cm\(^{-1}\); B,C - optical images (reflected light) of samples C(B) and D(C) with overlaid circles denoting individual Raman spectra acquisition points.

Crystalline phase presence in silicon films annealed with laser in presence of metal absorbing layer was confirmed using XRD analysis. Figure 3 presents part of annealed film XRD data that has a peak at 28.5\(^\circ\). This peak corresponds to crystalline silicon phase with orientation of (111). Average crystallite size estimated from XRD data is 24 nm.

Figure 3. XRD data of laser-annealed silicon film

4. Conclusions
A method for crystallized silicon films on flexible polymeric substrates is reported that combines advantages of widely used LIC and MILC approaches for low temperature crystallization of amorphous silicon. Necessity of buffer layer presence on substrate-silicon film interface is demonstrated experimentally. Whole silicon films with highly regular crystal structure and high
volumetric portion of crystalline phase are obtained, as confirmed by Raman and XRD measurements. Use of nickel and aluminum absorbing layers for inducing silicon crystallization is demonstrated.

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