

**Millisecond thermal processing using flash lamps for the advancement  
of thin layers and functional coatings**

Skorupa, W.; Schumann, T.; Rebohle, L.;

Originally published:

August 2016

**Surface & Coatings Technology 314(2017), 169-176**

DOI: <https://doi.org/10.1016/j.surfcoat.2016.08.010>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-23994>

Release of the secondary publication  
on the basis of the German Copyright Law § 38 Section 4.

CC BY-NC-ND

## Accepted Manuscript

Millisecond thermal processing using flash lamps for the advancement of thin layers and functional coatings

Wolfgang Skorupa, Thomas Schumann, Lars Rebohle

PII: S0257-8972(16)30734-4  
DOI: doi: [10.1016/j.surfcoat.2016.08.010](https://doi.org/10.1016/j.surfcoat.2016.08.010)  
Reference: SCT 21442

To appear in: *Surface & Coatings Technology*

Received date: 20 June 2016  
Revised date: 3 August 2016  
Accepted date: 4 August 2016



Please cite this article as: Wolfgang Skorupa, Thomas Schumann, Lars Rebohle, Millisecond thermal processing using flash lamps for the advancement of thin layers and functional coatings, *Surface & Coatings Technology* (2016), doi: [10.1016/j.surfcoat.2016.08.010](https://doi.org/10.1016/j.surfcoat.2016.08.010)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

## Millisecond thermal processing using flash lamps for the advancement of thin layers and functional coatings

Wolfgang Skorupa\*, Thomas Schumann and Lars Rebohle

Helmholtz-Zentrum Dresden – Rossendorf

Institute of Ion Beam Physics and Materials Research

Bautzner Landstraße 400, 01328 Dresden, Germany

\*E-mail: w.skorupa@hzdr.de

### Abstract

Thermal processing in the millisecond range provides advanced, non-equilibrium annealing techniques which allow dedicated material modifications at the surface without affecting the substrate volume below. The process called flash lamp annealing (FLA) is one of the most diverse methods of short time annealing with applications ranging from the classical field of semiconductor doping to the treatment of layers on glass, polymers and other flexible substrates. It still continues to extend to other material classes and applications, and becomes of interest for an increasing number of users. Other phrases for FLA used throughout the literature are intense pulsed light sintering (IPL) or photonic curing.

This review presents a short and comprehensive view of the current state of the art of FLA with a focus on functional coatings. After an introduction including historical aspects a look is taken to equipment issues as well as to the pioneering role which semiconductor processing in the framework of advanced chip technology played for the development of short time annealing. Mostly, examples of processing for photovoltaics, including doping aspects, hydrogen engineering, copper indium gallium diselenide (CIGS), silicon crystallisation on glass, and transparent conductive oxides (TCO), including indium tin oxide (ITO), zinc oxide (also Al-doped AZO) as well as inkjet printing for flexible electronics will be presented.

**Keywords:** flash lamp annealing (FLA), intense pulsed light sintering (IPL), semiconductors, silicon, indium tin oxide (ITO), ink jet printing,

## 1. Introduction

Short time annealing using light sources as a key method of thermal processing of semiconductors was firstly reported in 1975 by two Russian groups using lasers [1,2]. The first mentioning of flash lamp annealing (FLA) in the millisecond range was done by the Novosibirsk group [3 and personal communication]. Nevertheless, the modification of solid material by pulsed light treatments had already left behind a history which started earlier in the fifties [4].

The transition from the furnace with annealing times of several minutes up to hours and days to the laser with the chance to process materials in the pico- to nanosecond range led in the mid-seventies to fascination of scientists and engineers by seeing a new approach of modifying and manufacturing solid state materials. Foremost, real advancement for the most developed solid state technology, i.e. electronics on the micro- and nanoscale, was seen. First review papers on this topic appeared in the mid-eighties, e.g.[5,6]. During the late eighties and the nineties Rapid Thermal Processing (RTP) evolved to the leading technology developed for different aspects of the advanced semiconductor technology. The recent state of the art with an outlook to millisecond processing is reviewed in Refs. [7,8].

After this pioneering time, scientific and technological efforts led to a deeper understanding of the effects and mechanisms behind the different versions of short time annealing. Relatively independent of this revolutionary development devoted to microelectronic engineering a comparable approach, called intense pulsed light sintering (IPL) has been developing in the field of printed or low cost/large area electronics, firstly mentioned by Kim et al. [9]. Another phrase used for the same approach, called photonic curing, was claimed by Schroder with a trade mark [10,11]. A survey on the different short time annealing approaches is schematically shown in Fig. 1.

**Fig. 1:** Comparison of important parameters of different short time annealing techniques

Short time annealing processes allow for precise thermal treatment. Especially millisecond and nanosecond scale annealing using flash lamps and lasers are ahead in recent competition for numerous applications. Due to a short and highly energetic heat pulse only the near-surface region is being annealed which distinctly reduces the thermal budget on the substrate material. During the annealing time, the substrate only heats up gradually due to vertical heat diffusion up to an intermediate, comparatively low temperature and thus serves as a heat sink. This leads to a rapid cooling of the surface. Therefore the annealing time can

actively control diffusion and electrical activation of impurities, crystallization and other reordering processes. Moreover, the use of the liquid phase on the short time scale allows for extended opportunities of advanced processing. And this has also led to the use of fast thermal processing in more and more application niches, more and less away from the pioneering chip technology. Especially, thin layer engineering on both flexible and rigid substrate materials like glass, plastics, metals, paper, etc. got more and more into the focus of engineers.

In this short review several key applications and equipment issues of short time annealing will be discussed after this introduction. The focus will be finally on the engineering of thin layers mostly deposited on several substrate materials using flash lamps. More extensive reviews about the FLA topic from our group appeared elsewhere [12,13].

## **2. Equipment and processing**

The typical setup of a FLA tool as used for classical semiconductor wafer processing is schematically shown in Fig. 2. The wafer is processed in a chamber which can be flooded by an inert gas if needed and is supported by a holder made of quartz. A bank of halogen lamps below the wafer can be used to preheat the wafer which is needed to reduce strong temperature gradients between the back and the front side. This heating takes place on the time scale of seconds and is principally the same process as for RTP. The flash pulse itself is provided by a bank of flash lamps from the front side. Due to the high efficiency to convert electrical into optical energy Xe flash lamps with an internal gas pressure between 400 and 600 Torr are most commonly used. Under these conditions the lamps emit a broad spectrum from the UV to the near IR with a maximum in the blue spectral region. Thus, the adjustment of the FLA process to individual target materials is mainly performed by the specific choice of operation parameters like e.g. energy density, pulse duration or annealing ambient.

The reflector above the flash lamps directs the light toward the wafer and ensures a better homogeneity of the light on the wafer surface. For protection purposes the preheating and flash lamps are separated from the wafer by suitable quartz windows. More details about the basic technical features of FLA equipment and its operation like Xenon lamp issues, temperature distribution and measurement problems, strain and stress, outgassing, as well as reproducibility and homogeneity issues can be found in Ref.[13].

**Fig. 2:** Traditional setup of an FLA tool as used for semiconductor wafer processing.

The more recent development line is related to the thermal treatment of flexible or large area substrates by pulsed annealing (FLA or IPL or photonic curing). Flexible substrates demand a roll-to-roll transport system and have partly different requirements to the pulse annealing system. Normally, flexible substrates are processed in larger facilities which comprise several processing steps like deposition, patterning and annealing. Consequently, the pulse annealing tool is integrated into the processing line as a module, see Fig. 3a [14]. Depending on the required mode of irradiation, pulsed annealing can be performed in a continuous or camera mode [15]. In continuous mode (Fig. 3b), the whole area is annealed, but between two subsequent shots there is a small overlap zone where FLA has been applied twice. If this is not acceptable, FLA can be run in camera mode (Fig. 3c) where two subsequent shots are now separated by a small, but untreated stripe.

As the result of FLA processing strongly depends on the optical and thermodynamic properties of the material system, it is very difficult to give specific operation ranges for different material classes. However, one general tendency can be gained from the comparison of semiconductors with more temperature-sensitive substrates: whereas high annealing temperatures and relative long annealing times of several ms are often used in semiconductor applications, lower intensities at shorter annealing times (below 1 ms) and sometimes multiple FLA pulses are more common for temperature-sensitive substrates. In case of extremely temperature-sensitive substrates like polymer foils FLA is limited by the difference between the annealing temperature required on the front side and the maximum temperature the substrate can tolerate. If this difference is too large, the pulse time must be impractically short or additional thermal buffer layers have to be introduced to the system. Other limitations are materials which emit volatile components or easily bleach under strong light irradiation.

**Fig. 3:** Basic scheme of a FLA tool for roll-to-roll processes (a) Copyright 2015 John Wiley and Sons [14], FLA operation in continuous (b) and camera mode (c)

### 3. Doping of semiconductors - the driving force

This topic has been the most innovating one driving short time annealing to the present state of the art. The approach based on the annealing of ion implantation induced radiation damage due to nuclear and electronic excitation processes within semiconductor materials as silicon and germanium. The final goal is then the electrical activation of those atoms. [6,8]

The annealing temperature and time can actively control dopant diffusion and electrical activation, respectively. Short time annealing is a necessary prerequisite for shallow junction formation where strongly reduced diffusion without any loss of electrical activation is required. Moreover, advanced CMOS device technologies require the formation of ultra-shallow junctions in the source/drain extension regions which play a critical role in device characteristics. They do strongly influence the current drive capability and short-channel effects [16]. An important problem regarding the p-type doping with ion-implanted boron remains always the well-known effect of transient enhanced diffusion due to a silicon interstitial kick-out [17]. This problem can be solved applying shorter and shorter annealing times in combination with higher and higher temperature-time gradients during heating-up and cooling-down cycles. Also, pattern effects during chip processing have to be taken into account leading to a variation of optical properties across the patterned wafer surface [18]. A more recent review on that including also the aspects of millisecond and laser annealing was written by Paul Timans [19]. Recently, he demonstrated in detail specific applications for millisecond annealing during the fabrication of planar and FinFET-style CMOS transistors [8].

#### **4. Photovoltaics**

##### ***Doping***

The use of FLA was mainly driven by the need of damage annealing and electrical activation after ion implantation doping. On the other hand the community was reluctant to use this technology because of the cost factor, especially regarding beamline implantation. Only during the last 10-15 years the focus returned to this idea.

FLA related activities for photovoltaic applications were especially driven by a Japanese research group and the Rossendorf group. Ohdaira et al. concentrated on the crystallization of amorphous silicon on glass [20-26], see below. The Rossendorf group used FLA in a broader framework. A new technology with FLA as the key annealing step after doping by ion beam implantation or plasma immersion implantation was developed. FLA was used to simplify the fabrication process of dirty-silicon solar cells, especially by reducing the number of process steps, and paying attention to cost efficiency [27]. In this case an amorphous doped Si layer was the result of an ion beam phosphorus implantation step replacing the traditional  $\text{POCl}_3$  doping. In contrast to RTP and furnace annealing, FLA was able to successfully activate the dopants for the required sheet resistance range of solar cells

and to suppress the diffusion of metal impurities resulting in a distinct increase of the minority carrier diffusion length up to one order of magnitude (i.e. 80  $\mu\text{m}$  without surface passivation in this specific case). Further improvements were achieved by replacing the conventional ion beam implantation with the cost-effective plasma immersion ion implantation technique with a phosphine and hydrogen containing plasma [28]. Moreover, in this study the influence of FLA parameters and the annealing ambient on the hydrogen content and the minority carrier diffusion length was investigated in detail.

Normann et al. [29] and Riise et al. [30] investigated the in-diffusion of phosphorus and boron using spin-on deposition of a phosphorus and boron source, respectively, on the surface of monocrystalline silicon wafers followed by FLA as a feasible method to form high concentration shallow emitters for solar cells. By varying both the energy density of a 20 ms FLA step in the range from 62 to 132  $\text{Jcm}^{-2}$  and the sample preheating, it was observed that FLA treatments can in-diffuse a high concentration of phosphorus atoms that become electrically active. The most promising P-emitters were obtained after FLA in the energy range from 110 to 128  $\text{Jcm}^{-2}$  including preheating at 300  $^{\circ}\text{C}$  with a phosphorus concentration of  $4\text{-}6 \times 10^{20} \text{ cm}^{-3}$ . The emitter junction depth after these treatments is in the range of 100-200 nm. Sheet resistance values in the range of 60-100  $\text{Ohm/sq}$  were reached for both dopant types. For boron, optimum emitters were reached for energy densities below 105  $\text{Jcm}^{-2}$  for 10 or 20 ms annealing time leading to an emitter junction depth below 150 nm. For the boron case no preheating was needed. Like for the well-known case of boron implants, a transient enhanced diffusion effect was observed [17]. Here, the effect was explained by Si interstitial injection originating from a thermally activated reaction between the spin-on diffusant film and the silicon surface.

### **Thin silicon films on glass**

Generally, crystallization of thin silicon layers has been over many years a favorite topic for annealing schemes in the time range of seconds down to nanoseconds, mostly for flat panel active matrix liquid crystal displays. To realize low-cost large-area wafers, polycrystalline silicon is generally grown on cheap glass substrates. This is the same requirement if moving to photovoltaic applications because the cost factor is even more stringent there. A key requirement of the processing conditions is that temperatures in the glass do not exceed its softening point, which is around 600 $^{\circ}\text{C}$  for low-cost glass [31]. There are several established methods of film preparation that are compatible with this constraint on processing temperature. These are direct deposition of polycrystalline silicon and solid phase



crystallization or laser crystallization of amorphous silicon. Especially, the availability of the explosive crystallization scheme as well as the chance of operating in the liquid phase regime opened fascinating chances for materials modification. More detailed information about this topic it is found in Ref. [13].

Pioneering work by Pecz et al. [32] and Smith et al. [33] introduced the FLA application for this material in 2005. They investigated and modelled the crystallization of amorphous silicon (a-Si) layers by FLA. Intrinsic a-Si films with thickness in the range of 50-250 nm were deposited on glass and crystallized by FLA under different energy densities with a flash duration of 20 ms. Two different glass substrates were used for the deposition of a-Si films, Corning Code (CC) 7059 and CC 1737. Then a 100-nm thick SiO<sub>2</sub> layer was deposited by plasma enhanced chemical vapor deposition (PECVD) as protection layer on the glass, before the deposition of the a-Si film. The a-Si films were deposited by low-pressure chemical vapor deposition (LPCVD) at 420 °C, using disilane. They crystallized by forming grains with a mean size up to 6 μm almost free of within-grain defects. As for the case of Excimer laser processing, solid phase crystallization and super lateral growth were found to provide the growth mechanism. It was also demonstrated that FLA can successfully eliminate the within-grain defects in poly-Si films already crystallized by conventional low temperature furnace annealing [32]. The model by Smith et al. included both the thermal response of the wafers and the phase transition scenarios. Predictions from the model correlate well with existing experimental data and the model can be used to optimize process conditions [33]. The group of Ohdaira et al. investigated several aspects of the crystallization of amorphous Si layers for photovoltaic applications with thicknesses in the μm range in great detail, e.g. the influence of different substrates [21] or different deposition techniques [23,26].

The Korean group around S. Park devoted most of their activities to FLA of amorphous silicon layers on 500 μm thick glass substrates for display technology [34-38]. On top of the glass the following layer stack was arranged: 0.03 μm silicon nitride plus 0.3 μm silicon oxide plus 0.07 μm of amorphous silicon, all formed by PECVD. Aspects of boron and phosphorous doping as well as thermal warpage of the glass substrates and issues of scanning multi-shot irradiations were investigated. Of special interest are the considerations regarding the warpage of glass under FLA which continues the previous work by Smith et al. devoted to silicon wafer substrates [39].

One important issue for photovoltaics is the hydrogen handling, as on one side a low hydrogen content is desired in order to avoid crack formation or delamination during FLA, whereas on the other side hydrogen passivation is needed to achieve long minority carrier

lifetimes, as discussed in the paper of Bregolin et al. for the case of doping photovoltaic silicon [28]. Ohdaira et al. [22] reported that the surface region of about 500 nm of a 4.5  $\mu\text{m}$  thick film of a-Si deposited by catalytic CVD is rich in defects and voids after annealing by FLA using a 5 ms flash pulse. Minority carrier lifetimes below 10  $\mu\text{s}$  were measured, even after removing this surface region. The lifetime values improved after a subsequent high pressure vapour anneal, but the best properties were obtained after an additional post-FLA processing step, namely conventional furnace annealing at 450°C, see Fig. 4. The sharp increase in lifetime is explained by the enhanced dissociation of hydrogen molecules leading to an appropriate termination of dangling bonds. In contrast, the strong decrease for higher annealing temperatures is explained by an unwanted dissociation of Si-H bonds and out-diffusion of hydrogen.

Fig. 4: Minority carrier lifetime of a polycrystalline Si film as a function of the annealing temperature of post-FLA furnace annealing with an annealing time of 30 min in  $\text{N}_2$  ambient. Data taken from [22].

### **Copper indium gallium diselenide (CIGS)**

A novel process for the formation of copper indium gallium diselenide (CIGS) films was proposed by Dhage et al.[40, 41]. CIGS films with a thickness of 4 microns and grain sizes from 0.3 to 1 microns were prepared from a  $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})$  (CIG) metallic alloy and Se nanoparticles by the IPL technique. The melting of the CIG and Se nanoparticles and the nucleation of CIGS occurred in a very short reaction time of 2 ms. The authors assume that the Se diffuses into the CIG lattice to form the CIGS chalcopyrite crystal structure. Whereas these authors performed their experiments on conventional glass plates, another group reported recently also on IPL-treated CIGS-layers on flexible glass [42].

Another photovoltaic application of FLA was performed by Seeger et al.[43] and Reck et al.[44] for the improvement of the optical properties of copper–indium–(gallium)–sulphide films (CI(G)Su) and related chalcopyrites using zinc oxide films and FLA. The goal is the modification of the surface at the  $\text{Cu}(\text{In,Ga})\text{S}_2\text{-CdS}$  interface by preparing a shallow zinc profile without doping the whole absorber layer. Polycrystalline layers of such compound semiconductor materials with band gap energies that match well with the solar spectrum are suitable absorber layers for the thin film solar cell production [43].

## 5. Transparent conductive oxides (ITO, ZnO, AZO)

Dielectric or insulating layers also fall within the framework of our activities to use FLA as an advanced tool for creating new technological approaches. The very first activity was related to the ion beam synthesis of silicon dioxide by high dose oxygen implantation. Infrared spectroscopy was used to check the quality of the formed silicon oxide and whether a millisecond anneal step could create the same quality of the Si-O stretching band (wavenumber  $1075\text{ cm}^{-1}$ ) as the high-quality method of thermal oxidation used in microelectronic processing for gate oxides etc. Hensel et al. reported a successful FLA experiment already in 1985 [45] showing that the ideal wavenumber was reached for a layer with a stoichiometric oxygen dose by using an energy density of  $84\text{ J/cm}^2$  and a pulse time of 10 ms! During the last years also high-k dielectrics of the so-called second generation ( $\text{LaLuO}_3$  and  $\text{LaScO}_3$ ) were treated with FLA to avoid detrimental crystallization effects [46].

Regarding functional thin layer coatings for photovoltaics and low cost electronics the transparent conductive oxides (TCO) and inkjet-printed films are of much higher interest.

### Indium tin oxide (ITO)

ITO modification by FLA has been firstly demonstrated about ten years ago at the RTP conferences [15,47]. The main goal was the maximum decrease of the resistivity at highest transparency as usually required for such layers. The resistance of such inkjet-deposited layers could be decreased by about two orders of magnitude by just one flash. If there is too much energy introduced the layers may crack on a microscopic scale, see Fig.5. This leads finally again to an increase of the resistance.

Fig. 5: ITO layer with cracks on PET plastic foil taken with a light microscope

In order to ensure high quality TCO layer formation the deposition process has to be performed at a temperature higher than the recrystallization temperature. High deposition temperatures limit the number of possible substrates where the TCO could be used. Weller and Junghähnel have demonstrated crystalline, highly conductive ITO on ultra-thin glass using FLA to recrystallize the deposited ITO layer [14]. Glass substrates thinner than  $200\text{ }\mu\text{m}$  are flexible and allow for the use of roll-to-roll processing.

We demonstrated temperature distribution modelling for ITO-on-PET [15] and ITO-on-glass. Fig. 6 displays the simulated temperature distributions for 150 nm ITO on a 100  $\mu\text{m}$  glass foil for different depth regions and different pulse durations. In case of 20 ms there is little difference between the front- and backside of the foil, but as the pulse duration shortens this difference becomes larger. In addition, the energy density of the flash pulse necessary to achieve a certain surface temperature decreases. Thus, flash pulses shorter than 1 ms are especially suitable for flexible substrates. Furthermore, the present case of a transparent film on a transparent substrate is challenging as only the UV part of the flash lamp spectrum contributes to heating. The temperature trends in Fig. 6 are generally valid, but the specific energy density values are an overestimation. Firstly, the used ITO literature values for optical absorption lead to absorption of less than 5% in the ITO layer. Secondly, reflections at the chamber walls were not considered. Thus, in practical experiments as performed in [14] similar temperature profiles can be achieved with significantly lower energy densities.

Fig. 6: Temperature distribution in the system ITO-glass (150 nm thick ITO layer on a 100  $\mu\text{m}$  thick glass foil) for different flash pulses. The curves with the highest and lowest temperature represent the temperature profile at the front and back side, respectively, whereas the curve in between is the temperature profile 10  $\mu\text{m}$  below the surface.

Extensive work on FLA at ITO on glass backplanes was also done by Kim [48] using 0.4 ms flashes for 100 nm thick ITO layers on 500 micron thick glass reaching similar resistivity values as in case of glass foils [14]. Recently, Scherg-Kurmes et al. have shown that a FLA treatment for 2.7 ms of amorphous hydrogenated indium oxide ( $\text{In}_2\text{O}_3\text{:H}$ ) leads to the recrystallization independent of the substrate temperature during the deposition [49]. The recrystallized  $\text{In}_2\text{O}_3\text{:H}$  layer was polycrystalline with a carrier mobility higher than 100  $\text{cm}^2/\text{Vs}$  which is comparable to furnace annealing at about 180  $^\circ\text{C}$  for 15 min.

## ZnO

Gebel et al. [50] published the first results on FLA of zinc oxide layers. ZnO:Al films with a thickness of about 880nm that were deposited by magnetron sputtering. The glass substrate was not heated before or during or after the deposition. Subsequently the deposited layers

were treated by FLA at 1.3 ms. Using this method, the resistivity of the ZnO:Al films was decreased by a factor of two, down to  $1.0 \times 10^{-3}$  Ohmcm.

The microstructure revealed by cross-sectional transmission electron microscopy shows a typical preferred orientation of the c-axis perpendicular to the substrate surface, which is known for TCO layer growth (Fig. 7). There was basically no difference visible between the microstructure and the thickness of the as-deposited and the FLA-treated layer.

Fig. 7: XTEM micrograph of a FLA annealed AZO layer, after Gebel et al. [50]

Fig. 8: Optical band gap calculation for as-deposited and annealed ( $7.5 \text{ Jcm}^{-2}$ ) AZO layers, after Gebel et al. [50]

These results were in good agreement with those reported from rapid thermal processing or furnace annealing treatments. Despite the very short annealing time of only 1.3 ms not only the resistivity but also the transmittance in the UV and the blue spectral range were considerably improved. Fig. 8 shows the results of calculations regarding the band gap shift after FLA-treatment.

In another approach, plasma assisted reactive pulsed laser deposition followed by plasma immersion ion implantation of  $\text{SF}_6$  and post-implantation millisecond range FLA was used to fabricate nanocrystalline, highly n-type ZnO films on silicon wafers with superior properties [51]. The n-type doping was realised by the incorporation of F into the oxygen lattice site of ZnO and the efficient passivation of dangling bonds at grain boundaries. It was shown that during the FLA ( $35\text{--}50 \text{ J cm}^{-2}$ ) the fluorine is electrically activated and that the current-voltage characteristics reveal rectifying transport properties in the  $n^{++}\text{-ZnO:F/n-Si}$  structure. Moreover, the fluorine doping reduces the concentration of optically active defect centres. After annealing the ZnO films are fully recrystallized and maximum photoluminescence emission is obtained after annealing with a  $40 \text{ Jcm}^{-2}$ , 20 ms pulse. Annealing at higher energy leads to the degradation of film crystallinity and to a decrease of the photoluminescence emission.

Also, we investigated the effect of millisecond FLA on aluminum doped ZnO (AZO) films and their interface with a silicon wafer surface [52]. The AZO films were deposited by

magnetron sputtering on Si (100) substrates. The resistivity of the AZO film was reduced to a level close to the state-of-the-art value of  $2 \times 10^{-4}$  Ohmcm after FLA for 3 ms with an average energy density of  $29 \text{ J/cm}^2$ , a kind of optimum. Most of the interfacial defect energy levels were simultaneously annealed out, except for one persisting shallow level, tentatively assigned to the vacancy-oxygen complex in Si which was not affected by FLA. Subsequent to the FLA, the samples were treated in a  $\text{N}_2$  or forming gas ( $\text{N}_2/\text{H}_2$ , 90/10) atmosphere at 200-500 °C. The latter samples maintained the low resistivity values achieved after the FLA, but the former ones did not. The interfacial defect level persisting after the FLA is removed by the forming gas treatment, concurrently as another level emerges at  $\sim 0.18 \text{ eV}$  below the conduction band. The electrical data of the AZO films are correlated to point defects controlling the resistivity. It seems that the FLA may promote the formation of electrically neutral clusters of zinc vacancies rather than passivating/compensating complexes between the Al donors and the zinc vacancies. Impurity profiles of the interfacial region obtained by secondary ion mass spectrometry showed that there exist sensitive dependencies on the FLA energy density, as shown in Fig. 9. The dominating impurities in the AZO films are Al and H, rather homogeneously distributed to a depth of  $\sim 140 \text{ nm}$ . The H content is in the range of  $10^{18} \text{ cm}^{-3}$ , but about two orders of magnitude below that of Al, which appears as the clearly dominating shallow donor impurity. All other elements are estimated to be in the range of  $10^{17} \text{ cm}^{-3}$  or below. The interfacial redistribution starts for energy densities above  $\sim 37 \text{ J/cm}^2$  which causes a silicon in-diffusion into the AZO layer. Comparable effects were seen for oxygen (not shown) and Al, but also for Zn. This demonstrates a broadening of the interfacial region. At the same time, the amount of hydrogen decreases there.

Fig. 9: Depth profiles of Zn, Si, Al, and H determined by secondary ion mass spectrometry after FLA treatments using different energy density. Reprinted from [52] with the permission of AIP Publishing.

The improvement of the optical properties of copper–indium–(gallium)–sulphide films (CI(G)Su) and related chalcopyrites using zinc oxide films and FLA was described in the CIGS part of ch.4.

## 6. Flexible electronics and inkjet printing

Novel, flexible and low-cost electronic products with functionality far beyond that based on conventional size-restricted and rigid semiconductor devices require a rapid development of advanced material and preparation technology concepts. One of the most promising approaches to realize this ambitious goal is printed flexible as well as stretchable electronics (PFSE). A recent review was presented by Sigurd Wagner, one of the pioneers in this field. He wrote:

“Stretchable electronics is the newest class of large-area electronics. Quite literally large-area electronics has become a success story: flat panel displays are manufactured at the rate of 100 and solar cells at 200 square kilometers a year. Many of these products are made with thin films. Liquid-crystal displays are driven by active matrices of amorphous silicon transistors, 2 and 10% of all solar cells are made of amorphous silicon and chalcogenide films, respectively. Like any other stiff material, circuits become flexible and rollable when their thickness is reduced to 1/1000 of the desired radius of curvature. Thin film circuits are made on flat surfaces by standard microfabrication techniques. When made on plastic substrates and with plastically deformable interconnects, they can be shaped to surfaces that need expansion out of the plane, for instance spherical caps. On plastic substrates, this deformation is permanent. Elastomeric substrates and elastic interconnects let circuits go a shape beyond: to reversible deformation and near-arbitrary dimensions. Sizes and shapes of elastomeric circuits can be changed reversibly by applying mechanical force, by gas pressure, or by application of an electric field.” [53].

After 2006, in the framework of several projects with industrial partners, the Rossendorf group has been successfully using millisecond thermal processing by FLA as a highly-attractive technique for the functionalization of ITO-layers on glass and PET [15,47] as well as of copper and silver paste screen printed on low-thermal budget paper-like media for package labelling [unpublished results]. The effect of the FLA parameters (pulse duration, energy density) on the substrate behavior as well as on the microstructure and electrical response of the as-flashed films was studied. A significant drop of the sheet resistance of the FLA-treated layers as compared to the as-printed layers was observed. As FLA permits selective, near-surface heating, a damage of the sensitive substrates was avoided. The microstructure of the copper paste before and after FLA was also investigated. Fig. 10 shows the correlation between the achieved sheet resistance values and the corresponding microstructure of the copper paste films.

Fig. 10: Illustration of the distinct relation between the applied annealing conditions, evolution of the samples microstructure and resulting sheet resistance. Material studied: Cu-film/PET, No. 3. A) virgin material, B) as-flashed,  $E_D = 1.4 \text{ J/cm}^2$ , C) as-flashed,  $E_D = 1.75 \text{ J/cm}^2$  and D) as-flashed,  $E_D = 2.2 \text{ J/cm}^2$ . The pulse time was 600 microseconds.

More activities to use short time annealing after inkjet printing started in 2009 with a paper by Kim et al.[9]. Nittynen et al. compared recently the FLA with laser annealing (diode laser 808 nm) for the example of inkjet-printed copper nanoparticle layers [54]. A conductivity of more than 20% of that of bulk copper material has been obtained with both sintering methods. The authors consider both methods to be complementary techniques and highly suitable for this application field. Moreover, it was demonstrated by Yung et al.[55] that even a commercial camera flash device (in this case Nikon Speedlight SB-22) can be used for sintering of inkjet-printed silver tracks on polyimide, polyethylene terephthalate and photographic paper at room temperature. In this case the enhanced photothermal effect in silver nanoparticles was used.

More general, FLA processing of PFSE materials is a complex issue where the relevant processing parameters as pulse time and frequency, energy density, annealing ambient, preheating, and rear side cooling have to be carefully engineered for each specific application, see also ch.2. A good source of new information for this topic is the NIP & Digital Fabrication Conference [56]. Very recently, a topical review on low temperature thermal engineering of such ink applications for flexible electronics was published by S.H. Ko [57]. Printing has successfully demonstrated its potential for manufacture of advanced low-cost products (flexible displays, thin-film solar cells, large-area sensors etc.). Importantly, by using bendable, inexpensive media (e.g.: paper-like substrates, polymer films) and high-throughput roll-to-roll processing, a significant reduction of the overall costs has been achieved. Being highly-efficient (ultra-short), “non-destructive” (suitable for low-thermal tolerance flexible media) and compatible with roll-to-roll processing, FLA offers the realization of advanced PFSE products.

## 7. Concluding remarks



Although the basic effects regarding the use of energetic light pulses (lasers, flash lamps) were already explored in the mid-seventies, the real industrial applications started after 2000 in the advanced chip technology for engineering ultra-shallow junctions on silicon wafers. Meanwhile new fields of application came on stream using the main advantage of short energetic pulses in the time range of several milliseconds and lower. Especially, low cost electronics based on substrate materials like plastic foil, thin glass, cardboard, paper, etc. drive performance issues for equipment and processing. A number of convincing results have been reported during the last years. TCO layers as well as inkjet-printed patterns on such substrates need further attention from the R&D community, including further work on short time annealing approaches.

## References

- [1] G.A. Kachurin, N.B. Pridachin, L.S. Smirnov, Annealing of radiation defects by laser radiation pulses, *Sov. Phys. Semicond.* 9 (1975) 946.
- [2] E.I. Shtyrkov, I.B. Khaibullin, M.F. Galjautdinov, M.M. Zaripov, Ion-doped layer as a new material for recording holograms, *Optika i Spektroskopia* 5 (1975) 1031.
- [3] G.A. Kachurin, E.V. Nidaev, Effectiveness of annealing of implanted layers by millisecond laser pulses, *Sov. Phys. Semicond.* 11 (1977) 1178-1180.
- [4] M. Voelskow, R.A. Yankov, W. Skorupa, Historical aspects of subsecond thermal processing, in: W. Skorupa, H. Schmidt (Eds.), *Subsecond Annealing of Advanced Materials*, Springer Series in Materials Science **192** (2014) 1-13.
- [5] T.O. Sedgewick, Short time annealing, *J. Electrochem. Soc.* 130 (1983) 484-493.
- [6] C. Hill, Shallow junctions by ion implantation and rapid thermal annealing, *Nucl. Instr. Meth. B* 19-20 (1987) 348-58.
- [7] W. Lerch, J. Niess (eds.), *Rapid Thermal Processing and beyond: Applications in Semiconductor Processing*, *Mat. Sci. Forum* 573-574 (2008).
- [8] P.J. Timans, G. Xing, J. Cibere, S. Hamm, S. McCoy, Millisecond annealing for semiconductor device applications, in: W. Skorupa, H. Schmidt (Eds.), *Subsecond Annealing of Advanced Materials*, Springer Series in Materials Science **192** (2014) 229-70.
- [9] H.S. Kim, S.R. Dhage, D.E. Shim, H.T. Hahn, Intense pulsed light sintering of copper nanoink for printed electronics, *Appl. Phys. A* 97 (2009) 791-798.
- [10] K.A. Schroder, S.C. McCool, W.F. Furlan, Broadcast Photonic Curing of Metallic Nanoparticle Films, *Proc. NSTI-Nanotech Conf.* 2006, 3 (2006) 198-201.
- [11] K.A. Schroder, Mechanisms of Photonic Curing<sup>TM</sup>: Processing High Temperature Films on Low Temperature Substrates, *Proc. NSTI-Nanotech Conf.* 2011, 3 (2011) 220-223.

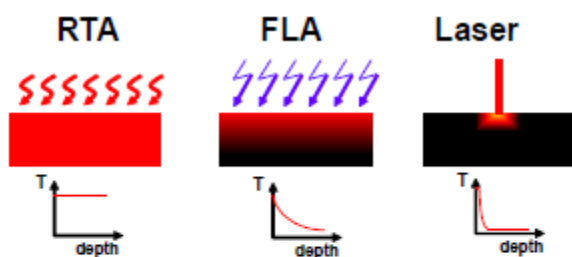
- [12] W. Skorupa, H. Schmidt (eds.), Subsecond thermal processing of Advanced Materials, Springer Series in Materials Science 192 (2014).
- [13] L. Rebohle, S. Prucnal, W. Skorupa, Thermal processing in the subsecond range: semiconductors and beyond, to be published.
- [14] S. Weller, M. Junghänel, Flash Lamp Annealing of ITO thin films on ultra-thin glass, *Vakuum in Forschung und Praxis* 27 (2015) 29-33.
- [15] T. Gebel, L. Rebohle, R. Fendler, W. Hentsch, W. Skorupa, M. Voelskow, W. Anwand, R.A. Yankov, Millisecond annealing with flash lamps: tool and process challenges, Proc. 14th IEEE Int. Conference on Advanced Thermal Processing of Semiconductors (2006) 47-55.
- [16] P.J. Timans, W. Lerch, J. Niess, S. Paul, N. Acharya, Z. Nenyeyi, Challenges for ultra-shallow junction formation technologies beyond the 90nm node, Proc. 11<sup>th</sup> IEEE International Conference on Advanced Thermal Processing of Semiconductors (2003) 17-33.
- [17] S.C. Jain, W. Schoenmaker, R. Lindsay, P.A. Stolk, S. Decoutere, M. Willander, H.E. Maes, Transient enhanced diffusion of B in Si, *J. Appl. Phys.*, 91 (2002) 8919-8941.
- [18] J. Niess, R. Berger, P.J. Timans, Z. Nenyeyi, Pattern effects and how to explore them, Proc. 10<sup>th</sup> IEEE International Conference on Advanced Thermal Processing of Semiconductors (2002) 49-57.
- [19] P.J. Timans, A Short History of Pattern Effects in Thermal Processing, *Materials Science Forum* 573-574 (2008) 355-74.
- [20] K. Ohdaira, S. Nishizaki, Y. Endo, T. Fujiwara, N. Usami, K. Nakajima, H. Matsumura, High-quality polycrystalline silicon films with minority carrier lifetimes over 5  $\mu$ s formed by flash lamp annealing of precursor amorphous silicon films prepared by catalytic chemical vapour deposition, *Jpn. J. Appl. Phys.* 46 (2007) 7198-7203.
- [21] K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, H. Matsumura, Formation of Several-Micrometer-Thick Polycrystalline Silicon Films on Soda Lime Glass by Flash Lamp Annealing, *Jpn. J. App. Phys.* 47 (2008) 8239-8242.
- [22] K. Ohdaira, H. Takemoto, K. Shiba, H. Matsumura, Drastic Improvement of Minority Carrier Lifetimes Observed in Hydrogen-Passivated Flash-Lamp-Crystallized Polycrystalline Silicon Films, *App. Phys. Expr.* 2 (2009) 061201.
- [23] K. Ohdaira, K. Shiba, H. Takemoto, T. Fujiwara, Y. Endo, S. Nishizaki, Y.R. Jang, H. Matsumura, Precursor Cat-CVD a-Si films for the formation of high-quality poly-Si films on glass substrates by flash lamp annealing *Thin Solid Films* 517 (2009) 3472-3475.
- [24] K. Ohdaira, T. Fujiwara, Y. Endo, S. Nishizaki, H. Matsumura, Explosive crystallization of amorphous silicon films by flash lamp annealing, *J. Appl. Phys.* 106 (2009) 044907.
- [25] K. Ohdaira, T. Fujiwara, Y. Endo, K. Shiba, H. Takemoto, H. Matsumura, Selection of Material for the Back Electrodes of Thin-Film Solar Cells Using Polycrystalline Silicon Films Formed by Flash Lamp Annealing, *Japan. J. App. Phys.* 49 (2010) 04DP04.

- [26] K. Ohdaira, N. Tomura, S. Ishii, H. Matsumura, Lateral Crystallization Velocity in Explosive Crystallization of Amorphous Silicon Films Induced by Flash Lamp Annealing, *Electrochemical and Solid State Letters* 14 (2011) H372-H374.
- [27] S. Prucnal, B. Abendroth, K. Krockert, K. Koenig, D. Henke, A. Kolitsch, H.J. Moeller, W. Skorupa, Millisecond annealing for advanced doping of dirty-silicon solar cells, *J. Appl. Phys.* 111 (2012) 123104.
- [28] F.L. Bregolin, K. Krockert, S. Prucnal, L. Vines, R. Huebner, B.G. Svensson, K. Wiesenhuetter, H.J. Moeller, W. Skorupa, Hydrogen engineering via plasma immersion ion implantation and flash lamp annealing in silicon-based solar cell substrates, *J. Appl. Phys.* 115 (2014) 064505.
- [29] B.H. Normann, L. Vines, V. Privitera, W. Skorupa, T. Schumann, B.G. Svensson, E.V. Monakhov, Phosphorus in-diffusion from a surface source by millisecond flash lamp annealing for shallow emitter solar cells, *Appl. Phys. Lett.* 102 (2013) 132108.
- [30] H.N. Riise, T. Schumann, A. Azarov, R. Hübner, W. Skorupa, B.G. Svensson, E.V. Monakhov, Formation of shallow boron emitters in crystalline silicon using flash lamp annealing: Role of excess silicon interstitials, *Applied Physics Letters* 107 (2015) 022105.
- [31] H. Kuriyama et al., Enlargement of poly-Si film grain size by excimer laser annealing and its application to high performance poly-Si thin film transistor, *Jpn. J. Appl. Phys.* 30, 12B (1991) 3700-3703.
- [32] B. Pecz, L. Dobos, D. Panknin, W. Skorupa, C. Lioutas, N. Vouroutzis, Crystallization of amorphous-Si films by flash lamp annealing, *Applied Surface Science* 242 (2005) 185-191.
- [33] M.P. Smith, R.A. McMahon, M. Voelskow, D. Panknin, W. Skorupa, Modelling of flash-lamp-induced crystallization of amorphous silicon thin films on glass, *J. Crystal Growth* 285 (2005) 249-260.
- [34] J.-W. Choi, W.-B. Jin, S.-M. Bae, Y.-H. You, H.-J. Kim, B.-K. Kim, Y. Kwon, S. Park, J.-H. Hwang, Rapid activation of phosphorous-implanted polycrystalline Si thin films on glass substrates using FLA, *ECS J. Science Technol.* 3 (2014) P391-P395.
- [35] W. Do, W.-B. Jin, J. Choi, S.-M. Bae, H.-J. Kim, B.-K. Kim, S. Park, J.-H. Hwang, Effect of FLA on electrical activation in boron-implanted polycrystalline Si thin films, *Mat. Research Bull.*, 58 (2014) 164-168.
- [36] W.-B. Jin, Y. Park, B.-K. Kim, H.J. Kim, J.-H. Hwang, H. Chung, J.H. Park, D.H. Kim, S. Park, Thermal warpage of a glass substrate during Xe-arc flash lamp crystallization of amorphous silicon thin-film, *Int. J. of Thermal Sciences* 83 (2014) 25-32.
- [37] J.-H. Hwang, H.J. Kim, B.-K. Kim, W.-B. Jin, Y. Kim, H. Chung, S. Park, Scanning multishot irradiations on large-area glass substrate for Xe-Arc flash lamp crystallisation on amorphous silicon-film, *Int. J. Thermal Sciences* 91 (2015) 1-11.

- [38] D.-H. Kim, B.-K. Kim, H.J. Kim, S. Park, Crystallisation of amorphous silicon thin-film on glass substrate preheated at 650°C using Xe arc flash of 400 microseconds, *Thin Solid Films* 520 (2012) 6581-6588.
- [39] M.P. Smith, K.A. Seffen, R.A. McMahon, M. Voelskow, W. Skorupa, Analysis of wafer stresses during millisecond thermal processing, *J. Appl. Phys.* 100 (2006) 063515.
- [40] S.R. Dhage and H.T. Hahn, Rapid treatment of CIGS particles by intense pulsed light, *J.Phys.Chem.Solids* 71 (2010) 1480-1483.
- [41] S.R. Dhage, H.S. Kim, H.T. Hahn, Cu(In,Ga)Se<sub>2</sub> Thin Film Preparation from a Cu(In,Ga) Metallic Alloy and Se Nanoparticles by an Intense Pulsed Light Technique, *J. Electronic Materials* 40 (2011) 122-126.
- [42] A.C. Badgajar, K. Madhuri, S. Garner, S.R. Dhage, S.V. Joshi, Proc. 42th IEEE Photovoltaic Specialist Conference (2015) 1-4.
- [43] S. Seeger, K. Ellmer, J. Reck, J. Schulte, P. Helm, Modification of the surface of Cu(In,Ga)S<sub>2</sub> absorbers by shallow Zn-profiles, Proc. 28th European Photovoltaic Solar Energy Conference and Exhibition, Paris (2013) 2463-2466.
- [44] J. Reck, S. Seeger, M. Weise, R. Mientus, J. Schulte, K. Ellmer, Flash-lamp annealing of ZnO-layers on copper-indium-gallium-sulphide layers: A spectroscopic ellipsometry study, *Thin Solid Films* 571 (2014) 762-766.
- [45] E. Hensel, K. Wollschläger, D. Schulze, U. Kreissig, W. Skorupa, J. Finster, Si-O compound formation by oxygen ion implantation into silicon, *Surf. Interf. Analysis* 7 (1985) 207-210.
- [46] J. Lehmann, R. Hübner, J. von Borany, W. Skorupa, T. Mikolajick, A. Schäfer, J. Schubert, S. Mantl, Millisecond flash lamp annealing for LaLuO<sub>3</sub> and LaScO<sub>3</sub> high-k dielectrics, *Microelectronic Engineering* 109 (2013) 381-384.
- [47] W. Skorupa et al., Millisecond beyond chip technology: From electronics to photonics, Proc. 15th IEEE Int. Conference on Advanced Thermal Processing of Semiconductors (2007) 47-55.
- [48] Y. Kim, S. Park, B. K. Kim, H.J. Kim, J. H. Hwang, Xe-arc flash annealing of indium tin oxide thin-films prepared on glass backplanes International, *J. Heat and Mass Transfer* 91 (2015) 543-551.
- [49] H. Scherg-Kurmes, S. Seeger, S. Körner, B. Rech, R. Schlatmann, B. Szyszka, Optimization of the post-deposition annealing process of high-mobility In<sub>2</sub>O<sub>3</sub>:H for photovoltaic applications, *Thin Solid Films* 599 (2016) 78-83.
- [50] T. Gebel, M. Neubert, R. Endler, J. Weber, M. Vinnichenko, A. Kolitsch, W. Skorupa, H. Liepack, Millisecond-annealing using flash lamps for improved performance of AZO layers, *Mat. Res. Soc. Symp. Proc.*, 1287 (2011) mrsf10-1287-f10-10, doi:10.1557/opl.2011.1438.

- [51] S. Prucnal, K. Gao, S.Q. Zhou, J. Wu, H. Cai, O. Gordan, D.R.T. Zahn, G. Larkin, M. Helm, W. Skorupa, Optoelectronic properties of ZnO film on silicon after SF<sub>6</sub> plasma treatment and milliseconds annealing, *Appl. Phys. Lett.* 105 (2014) 221903.
- [52] P.F. Lindberg, F.L. Bregolin, K. Wiesenhütter, U. Wiesenhütter, H.N. Riise, L. Vines, S. Prucnal, W. Skorupa, B.G. Svensson E.V. Monakhov, The effect of millisecond flash lamp annealing on electrical and structural properties of ZnO:Al/Si structures, *J. Appl. Phys.* 119 (2016) 185305.
- [53] S. Wagner, S. Bauer, Materials for stretchable electronics, *MRS Bulletin* 37 (2012) 207-217.
- [54] J. Niittynen, E. Sowade, H. Kang, R.R. Baumann, M. Mantysalo, Comparison of laser and intense pulsed light sintering (IPL) for inkjet-printed copper nanoparticle layers, *Scientific Reports* 5 (2015) 8832.
- [55] K.C. Yung, X. Gu, C.P. Lee, H.S. Choy, Ink-jet printing and camera flash sintering of silver tracks on different substrates, *Journal of Materials Processing Technology* 210 (2010) 2268-2272.
- [56] NIP & Digital Fabrication Conference, <http://www.ingentaconnect.com/content/ist/nipdf> (accessed May 24, 2016).
- [57] S.H. Ko, Low temperature thermal engineering of nanoparticle ink for flexible electronics applications, *Semicond. Sc. Technol.* 31 (2016) 073003.

Figure 1



backside	hot	cold	at RT
annealing times	1 – 100 s	100 $\mu$ s – 100 ms	1 – 1000 ns
light source	halogen lamps	Xe lamps	pulsed laser
spectrum	broad ~ 800 nm	broad ~ 400 nm	discrete lines
pattern effects	not significant	significant, but reduced	significant
operation mode	wafer by wafer	wafer by wafer	wafer scanning

Figure 2

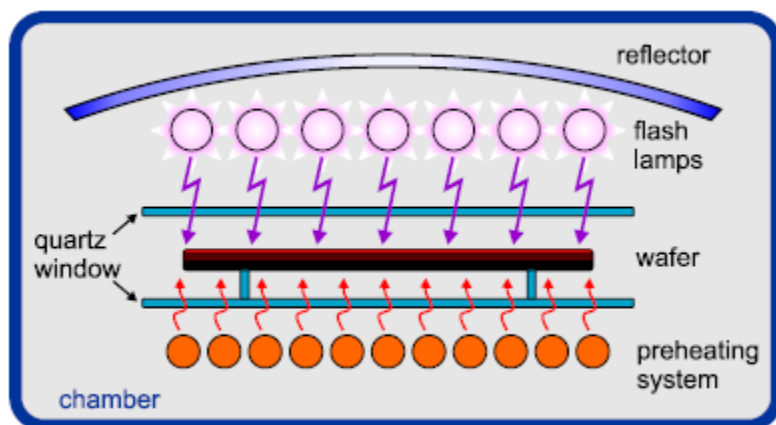


Figure 3

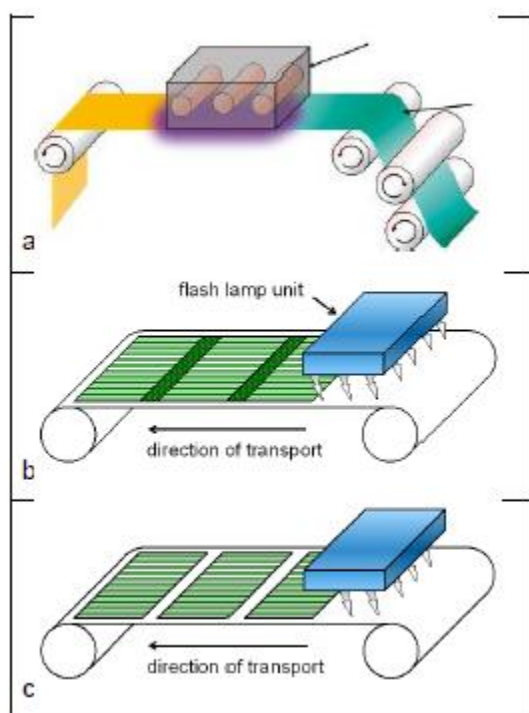
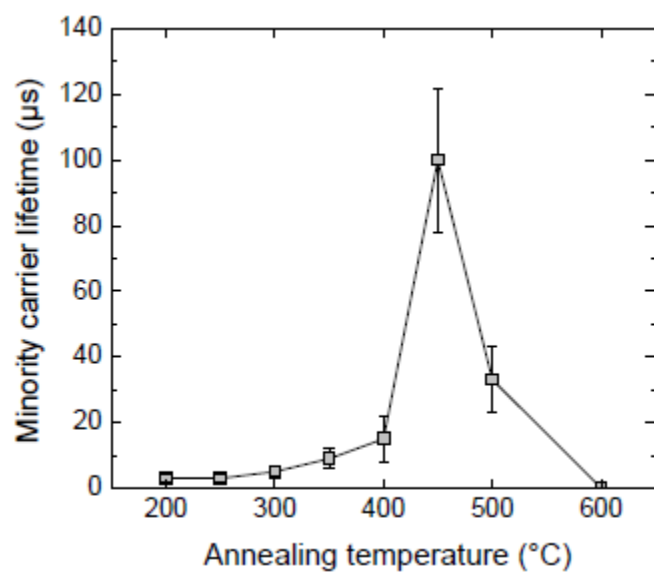
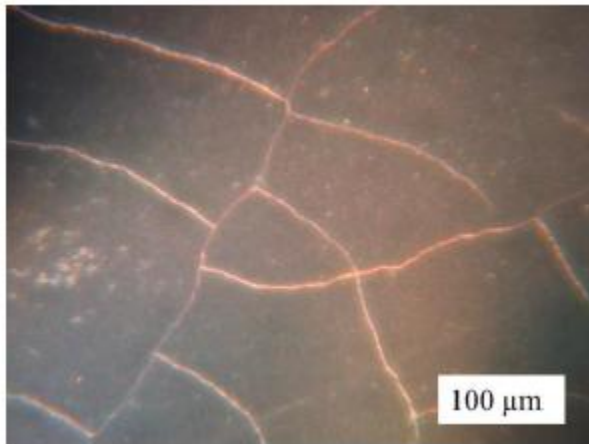




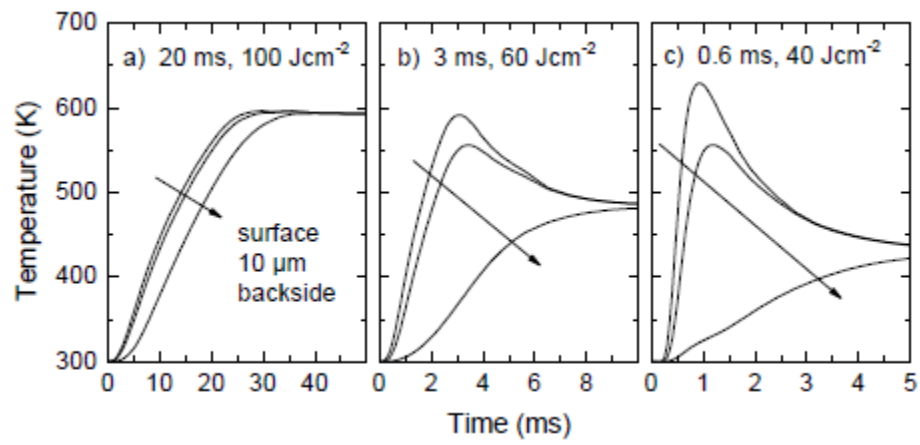
Figure 4

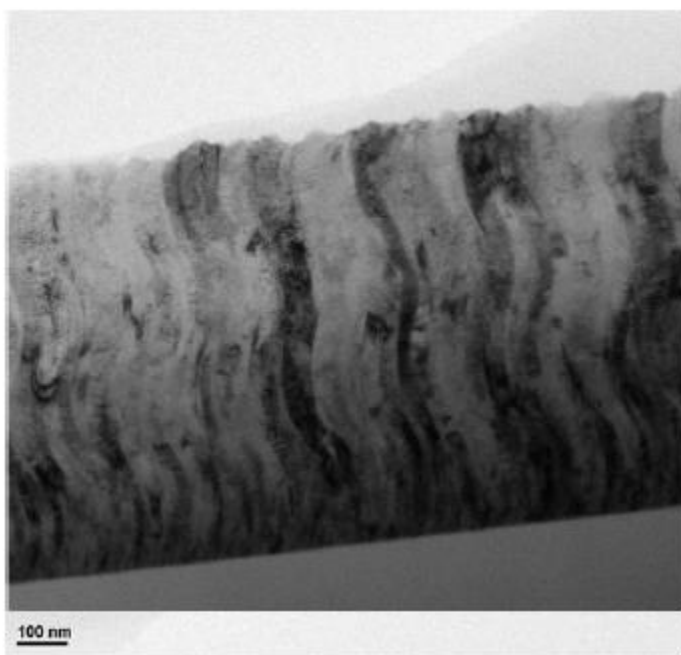


**Figure 5**

ACCEPTED MANUSCRIPT

Figure 6



**Figure 7**

ACCEPTED

SCRIPT

Figure 8

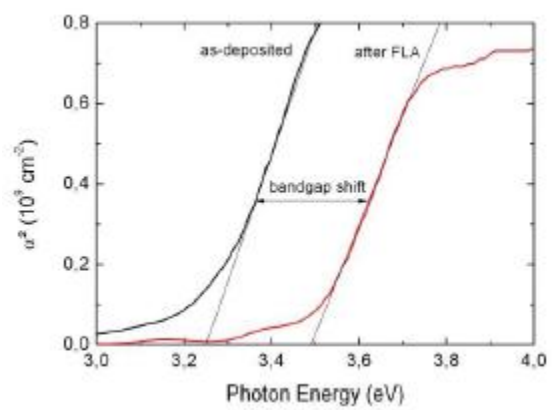


Figure 9

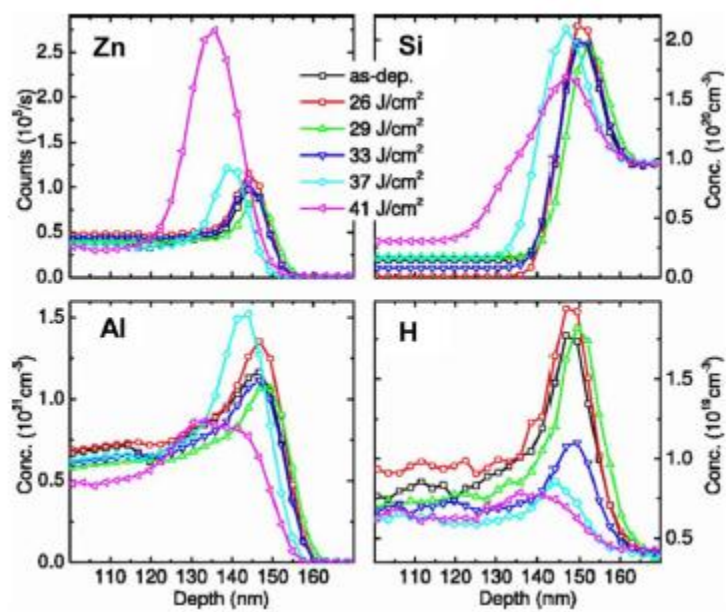
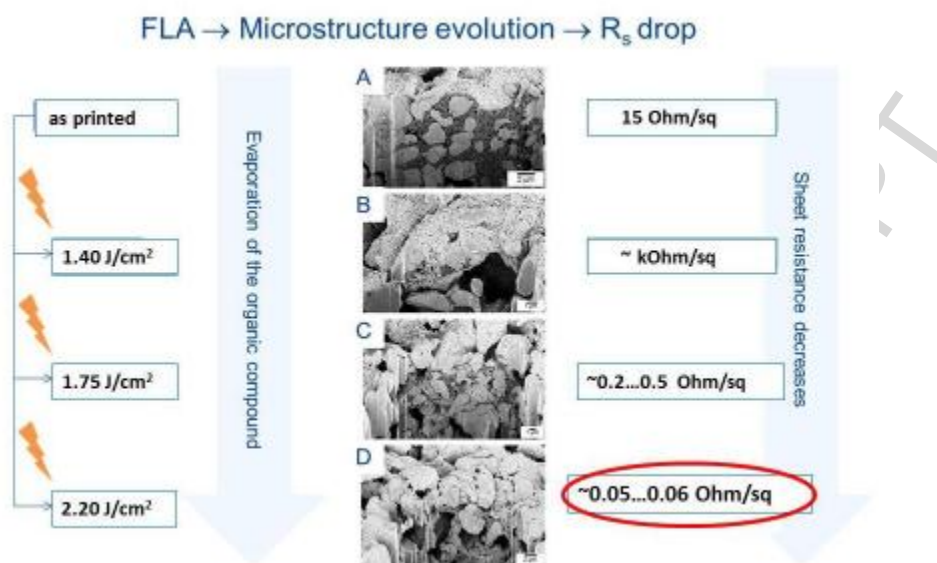


Figure 10



**Highlights**

W3-SVC 2016 (W.Skorupa)

flash lamp annealing (FLA),

intense pulsed light sintering (IPL),

semiconductors,

silicon,

indium tin oxide (ITO),

ink jet printing

ACCEPTED MANUSCRIPT