Nano electron field emitters synthesized using excimer laser assisted metal induced crystallization of thin silicon films

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Hydrogenated amorphous thin silicon films (a-Si:H) deposited using Plasma Enhanced Chemical Vapor Deposition (PECVD) on metal coated glass substrates were investigated to analyze the effect of a novel processing technique known as Laser Assisted Metal Induced Crystallization (LAMIC) on their Electron Field Emission (FE) properties. Post-surface characterization of the processed LAMIC thin silicon films showed increased surface roughness and the presence of uniformly spaced "island-like" micro-nano structures on the surface of metal coated backplane samples. Best diode configuration FE results were obtained from samples sputtered with a thin layer of aluminum (Al) on top and cross laser annealed at 190 mJ/cm^2 (y-axis) and 100 mJ/cm^2 (x-axis). FE currents were measured as high as 12 μA at emission thresholds of 8–30 V/μm. FE results of the LAMIC thin silicon films were found to be particularly dependent on laser fluence and the surface morphology exhibited very high discharge resistance. Oxidation of LAMIC films was observed to deteriorate the FE characteristics, thereby increasing the emission threshold to 30–35 V/μm. Finally, a hybrid emission model has been proposed that explains the electron emission from such LAMIC thin silicon films.

(Received September 7, 2018; accepted April 9, 2020)

Keywords: Hydrogenated amorphous silicon, Plasma enhanced chemical vapor deposition, Excimer laser assisted metal induced crystallization, Nanostructures, Electron field emission display

1. Introduction

Flat panel display industry is one of the most prominent technologies in today's market and is estimated to be around \$100bn. Liquid crystal display (LCD) technology has mostly resolved most of the display problems and is currently the dominant mass market consumer display. However, LCD technology has some limitations such as low contrast levels (due to backlight) that are evident for certain applications such as true video rendering of images. New emissive display technologies such organic light emitting diodes (OLED) are making inroads, however they too suffer from issues such as screen burn-in and degradation in light output over period of time. Field Emission Displays (FED) have been investigated for some time and have long been considered an ideal candidate for flat panel display due to its emissive nature, low power, high speed and true color reproduction. Earlier devices exploited the geometric confinement of electric fields at fabricated sharp electron emitter micro-tips producing high local fields at low voltages. This allowed for quantum mechanical tunneling of electrons from the emitter tips into vacuum. Earlier prototype devices were fabricated using metallic emitter tips and were developed by Spindt during the 1960/70s, forming the foundation of the modern FED [1]. Field emission devices based on microelectronically fabricated silicon electron emitters have also been studied. But due to high manufacturing cost and emission uniformity issues, they have been ruled out for mass market application. Some recent studies have demonstrated electron emission at low field emission thresholds from planar devices, thereby not requiring any expensive fabrication of emission structures.

Field emission from such devices can be explained using the popular Fowler-Nordheim (F-N) model, that governs the relationship between emission current density, work function and the applied electric field based on tunneling of electrons through a triangular barrier [2,3]. The F-N equation can be used for creating Fowler Nordheim plots that allows us to determine the β factor, which becomes unusually high for certain configuration of FE devices. Here, β is the field enhancement factor, E is applied field and φ is the work function.

$$I = \alpha E^2 \exp\left(\frac{-b\varphi^{\frac{3}{2}}}{\beta E}\right) \quad (1)$$

Due to the problems faced by earlier field emission devices, carbon nanotubes (CNTs) were considered as the ideal emitters, due to very high aspect ratio and mechanical stability at high electric fields. But concerns such as stray dominant emitters and proximity effects made them difficult to control and mass produce due to very low yield. Promising FE thresholds have also been observed from amorphous carbon [4], diamond like carbon [5], planar amorphous silicon [4] and microcrystalline

silicon [6]. Filamentary conduction in thin silicon films [7-10] has reported stable field emission currents after a break-down within the film. This process is known as "conditioning", which results in the formation of stable conducting filaments within the thin films, thus allowing for high emission current densities and quantized resistance. Silva et al. has demonstrated that conditioning of thin silicon films using current-stressing resulted in structural changes in the films, thus allowing for very low FE emission thresholds [4]. Our contribution in this paper is as follows.

- We have demonstrated a novel processing technique based on pulsed excimer laser assisted metal induced crystallization to synthesize lithography free micro-nano electron field emitters from thin silicon films.
- Samples fabricated with the LAMIC processing technique were measured to have FE currents as high as 12 μA at emission thresholds of 8 – 30 V/μm.
- Post oxidation of LAMIC processed films has been attributed to increase in the emission threshold.
- A hybrid model for electron emission from LAMIC processed thin silicon films has been proposed.

2. Laser Assisted Metal Induced Crystallization of PECVD thin silicon films

Recent studies have shown that laser crystallization (LC) of a-Si:H produces a roughened surface that gives excellent field emission properties [11]. Amorphous silicon grown under standard conditions for thin film transistors (TFT's) is deposited on metal backplane corning glass substrates. When processed in air using a pulsed krypton fluoride (KrF) excimer laser at a wavelength of 248 nm, the as-deposited thin silicon film, with 10% hydrogen content produces conical micro-nano structures on its surface. This surface is highly dependent on the laser parameters such as beam shape, laser fluence, scan speed. In our earlier study [12], we have also demonstrated that field emission can also be achieved using aluminum induced crystallization (AIC) of a-Si:H thin silicon films using isothermal heating. However, issues such as very long thermal annealing times, lack of uniformity in surface crystallization/roughening and non-uniformity in field emission currents made it difficult to control. In this study, we amalgamated the above two processing techniques, i.e. LC and AIC, and developed a novel processing technique called LAMIC to address the non-uniformity issues mentioned for AIC isothermal annealing process. Using the LAMIC process, we significantly reduced the annealing time, and uniformity in surface annealing was maintained due to the use of a homogenized laser beam. As shown in Fig.1, Corning 7059 glass substrates were first coated with Al backplane metal of thickness ~100 nm using d. c. magnetron sputtering process. Undoped thin silicon film samples of thickness (~100 nm) were then deposited using standard PECVD technique. Deposition was carried out at a substrate temperature of 250 °C, RF power of 6.5 W and deposition pressure of 150 mtorr, silane with hydrogen dilution (H_2/SiH_4) ratio maintained at 20 % and the gas flow rate was fixed to 100 sccm. Hydrogen content in the deposited thin films was measured at ~10 %. No dehydrogenation or pre-baking steps were done prior to LAMIC processing. The samples were finally coated with a very thin layer of Al (~ 3 to 5 nm) on top using d. c. magnetron sputtering process.

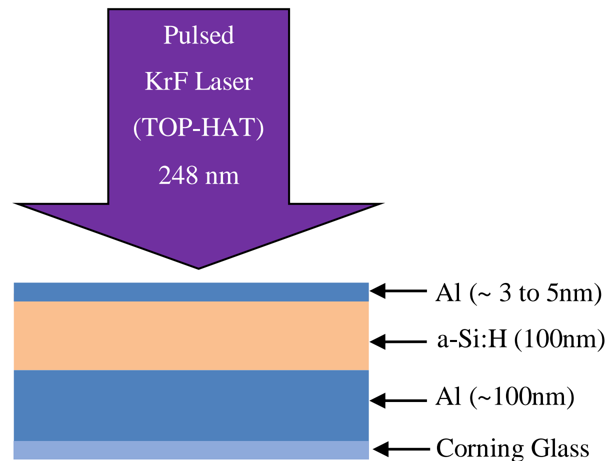

Fig. 1. Top-Hat beam profile of the 248 nm, 4×10 mm² laser pulse. Dimensions measured at the sample plane (color online)

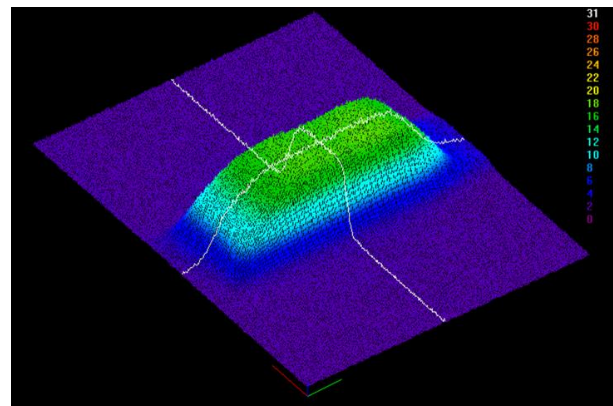

Fig. 2. Top-Hat beam profile of the 248 nm, 4×10 mm² laser pulse. Dimensions measured at the sample plane

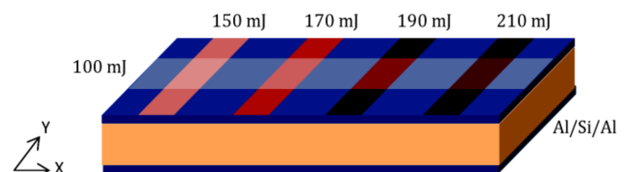

Fig. 3. Schematic diagram of different laser fluence energies and scan directions (color online)

Samples were then excimer laser annealed in air using a "Top-Hat" beam profile (Fig. 2) with 4×10 mm² footprint using fluence ranging from 150 to 210 mJ/cm² in steps of 20 mJ at 20 Hz in the Y direction and then at 100 mJ/cm² at 20 Hz in the X direction, as shown in Fig. 3. This was a slight deviation from the existing laser

annealing process and was done to investigate the effect of crossed laser annealing on the surface morphology and field emission threshold of the thin silicon films. LAMIC processing of the developed samples was performed at a scan rate of 2 mm/s on a moving X-Y stage whose traverse speed modified the frequency of laser beam seen by the samples. It was observed that by controlling the laser fluence, scan speed and beam profile, we were able to fabricate uniform micro/nano structures on the surface of the thin films.

LAMIC processing of thin silicon films allows for uniform distribution of heat over the exposed area of the thin film. This maintains uniformity in the crystallization of the films, an issue that was highlighted in the isothermal annealing process [12]. It was also observed that laser processing in air also effects the composition and structure of the resultant film. During processing, the samples are exposed to temperatures near to the ablation limit, this causes melting of the thin silicon film. The initial laser pulse would melt/quench silicon and dehydrogenate the film, thereby changing its absorption co-efficient.

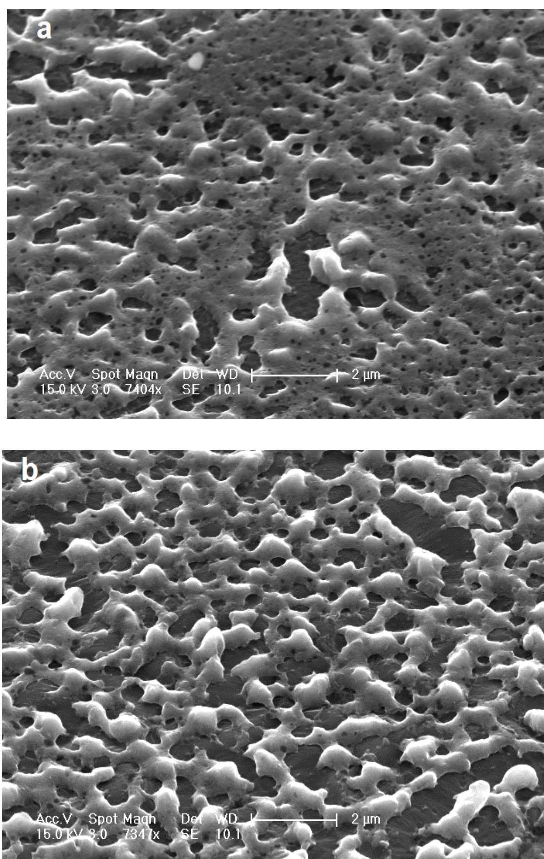

Fig. 4. SEM micrograph of LAMIC thin silicon film annealed at a) 190 mJ/cm^2 and b) 190 + 100 mJ/cm^2

This cycle continues with the following pulses, thereby creating a unique internal structure in the resultant material. Surface profiling of the processed samples was performed using JEOL 6310 for scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDAX-Spectra) for elemental mapping of the LAMIC thin silicon films. Diode configuration FE measurements were conducted using a stainless steel spherical anode probe (~5 mm in diameter). The spherical anode probe is mounted on a piezo-ceramic actuator that allows movement of the probe in sub-micron steps. The anode probe is positioned above the sample (cathode) at a height of 50 µm from the surface. The applied electric field is increased every 30 sec and the resulting current measurements were recorded. The electron field emission threshold is defined as the applied macroscopic field that produces a steady emission current not less than 1nA. Planar anodes coated with indium tin oxide (ITO) and green phosphor have also been used to observe light emission from the LAMIC thin silicon films. FE tests were carried out in a vacuum better than 2×10^{-6} mbar.

2.1. Surface characterization of LAMIC thin silicon films

Initially it was expected that using a pulsed laser beam for annealing thin silicon films coated with Al would not be very effective due to reflections caused by the very thin Al layer on top of silicon. However, this turned out not to be the case. It was seen that areas coated with Al on top crystallized more readily than the areas laser annealed without the Al layer with energy fluence's below the melt threshold of silicon. This can be understood due to the presence of Al which catalyses crystallization of silicon in air. Samples only annealed in the vertical Y-direction fluence's looked like melted silicon-aluminium slurry (Fig. 4a), whereas post-annealing of these areas with a horizontal X-direction cross-over fluence of 100 mJ/cm^2 was seen to modify the surface morphology of the thin silicon films to to form interconnected micro-nano structures (Fig. 4b). Typically a low energy pulse of a 100 mJ/cm^2 would hardly induce any surface change on the thin silicon films. However, with 3 to 5 nm of Al on top, significant surface changes were observed. From Fig. 5, we can see that over the entire laser annealed range, the highest features are formed at sample annealed using 190+100 mJ/cm^2.

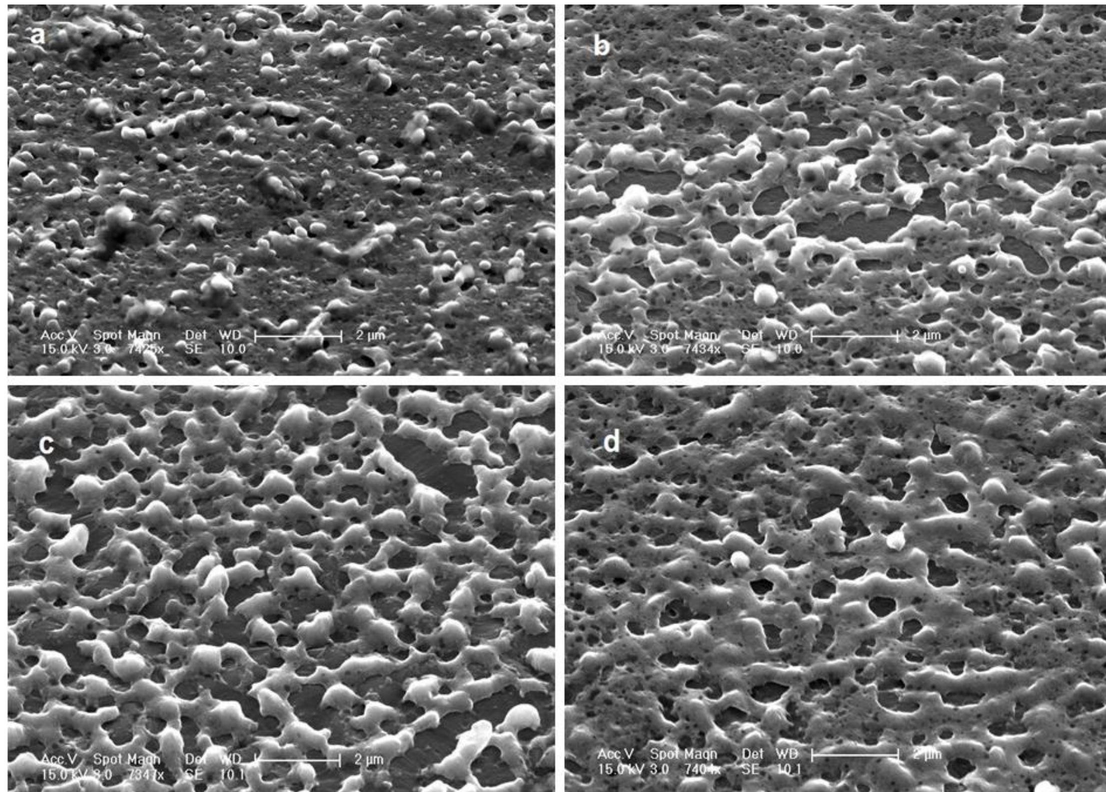

Fig. 5. SEM micrograph of LAMIC thin silicon films annealed at a) 150+100 mJ/cm², b) 170+100 mJ/cm², c) 190+100 mJ/cm² and d) 210+100 mJ/cm²

2.2. Electron field emission measurements from LAMIC thin silicon films

Processed samples were tested for field emission initially using anode probe current measurements (Fig. 6) then later using the phosphor coated anode plate for light emission test (Fig. 7). The best and consistent field emission results were obtained from samples annealed at 190+100 mJ/cm² annealed area (Fig. 5c). The conditioning threshold for FE was measured between 20-25 V/µm. Following this initial conditioning stage a repeatable field emission curve can be shown that has thresholds (field required for 1nA) of between 8-12 V/µm, better than some earlier reported emission thresholds of 10-20 V/µm from thin amorphous silicon films [4]. The results obtained here can be reproduced uniformly across the entire area processed with the same laser regime and repeatable over the cycled up and cycled down applied electric field (Fig. 6). Maximum emission current has been measured at 12 µA at a field of 30 V/µm.

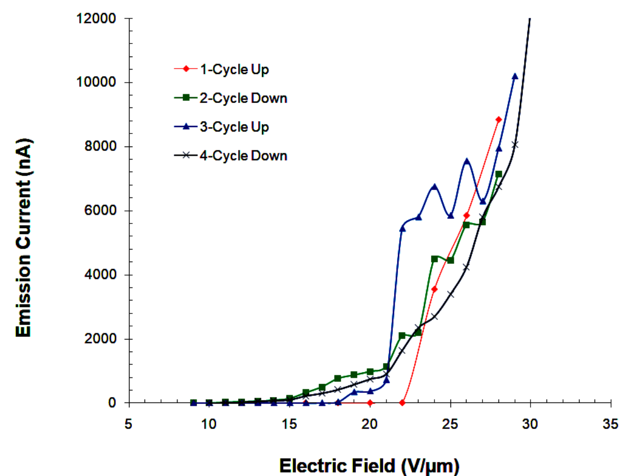

Fig. 6. FE plot of LAMIC thin silicon film annealed at 190+100 mJ/cm² at 50 µm anode-cathode gap (color online)

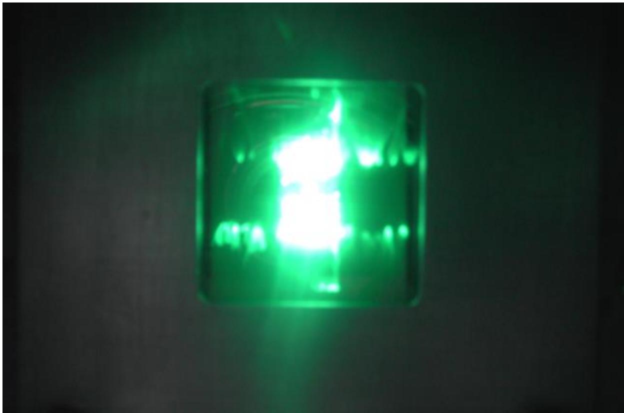

Fig. 7. Light emission from LAMIC thin silicon film annealed at 190+100 mJ/cm² tested using an ITO coated phosphor anode plate in vacuum (color online)

No modification of the sample surface was observed following FE tests, suggesting high discharge resistance due to chemical stability of the Al-Si silicide layer formed on the surface after LAMIC processing, an issue that plagued some earlier emitters [4, 6].

2.3. Effect of oxidation on FE characteristic of LAMIC thin silicon films

LAMIC samples annealed at 190+100 mJ/cm² were re-tested after 1 month exposure to air; deterioration in the field emission threshold was observed (Fig. 8). The emission threshold increased to 30–35 V/µm, but was seen to be still uniform across the sample surface. No evidence of a high field conditioning step was observed. This could be because these emission sites were already conditioned a month before in the earlier field emission tests (Fig. 6).

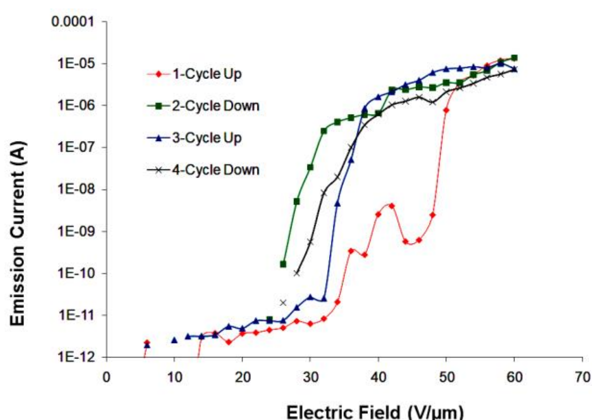

Fig. 8. FE plot of film annealed at 190+100 mJ/cm² at 50 µm anode-cathode gap tested after 1 month exposure to air (color online)

This high emission threshold was attributed to the formation of an oxide layer on the sample surface that reduced the field emission performance of the sample. This was confirmed from the composition analysis using EDAX-Spectra, which revealed the presence of oxygen within the sample. (Fig. 9).

3. Model of field emission from LAMIC thin silicon films

FE from these samples cannot be attributed only to geometric field enhancement, due to absence of any significant surface features. Although emission from such planar films can be fitted to a Fowler-Nordheim curve, but the obtained values for such flat films are unrealistic. Hence an internal field enhancement mechanism due to the formation of a Al-Si silicide top layer after LAMIC processing and the presence of highly conducting nanostructures within the bulk of the thin film must have a significant effect on electron emission, due to work function lowering and filamentary conduction respectively. Amaratunga and Silva have shown in the past that low electron emission (1–10 V/µm) can occur even from atomically flat surfaces (flat to within a couple of nanometers, as measured by scanning probe techniques) [5], hence emission from the LAMIC thin silicon films cannot be exclusively due to external geometric field enhancement. Forbes et al. suggest that electrically conducting nanostructures inside the thin films can create field enhancement at the surface/vacuum interface, thereby creating a local field significantly greater than the macroscopic field that can allow electron tunneling into vacuum [13].

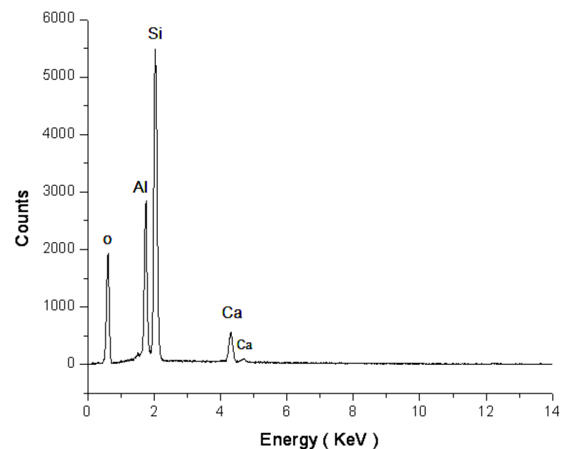

Fig. 9. EDAX Spectra of LAMIC thin silicon film annealed at 190+100 mJ/cm² and tested after 1 month exposure to air

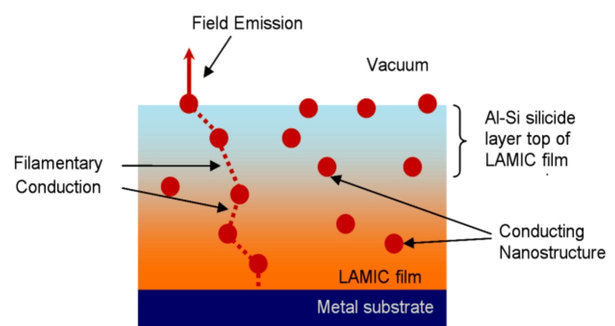

Fig. 10. Schematic diagram of a model of a hybrid conduction mechanism in LAMIC processed thin dielectric films (color online)

These randomly distributed conducting nanostructures within the bulk of the thin film under an applied electric field (responsible for guiding the electrons) form stable filamentary one-dimensional conducting channels between them that allow electrons to tunnel/hop between the nanostructures and finally escape into the vacuum (Fig. 10). The distribution/spacing of these nanostructures determines the tunneling current, which increases with decreasing nanostructures spacing [13].

Chung et al. used a band model to describe the emission process from metal silicides. It is suggested that a thin metal silicide layer on top of the silicon layer acts as a metal-rich layer with metal-like electrical properties with a very low work function [14]. Further, excimer laser annealing of Al/Si thin films form regions of highly doped p-type silicon layer. P-type silicon emits at a lower extraction voltage compared to n-type silicon, as n-type silicon are negatively charged and form a potential barrier against electrons and hence a much stronger field would be needed for electrons to tunnel into vacuum [15,16]. Hence in our LAMIC thin films when the electrons from the bulk silicon flow to the Al-Si silicide top layer, due to the lower work function they are able to tunnel easily through the vacuum barrier. From these observations we can speculate that an overall field enhancement from LAMIC processed thin silicon films is a hybrid process of geometric field enhancement (conducting particles protruding from the surface) and internal field enhancement (top Al-Si silicide layer work function lowering and conducting nanostructures within the dielectric thin film) factors.

4. Conclusion

A novel processing technique based on pulsed excimer laser assisted metal induced crystallization of thin silicon films has been successfully demonstrated to synthesize lithography free micro-nano electron emitters from thin silicon films for field emission display application. LAMIC samples demonstrated high emission currents at low emission thresholds, large area emission uniformity and very high discharge resistance. Post oxidation field emission thresholds were observed to be higher compared to pre-oxidation field emission thresholds. This was attributed to the presence of oxygen in the samples as confirmed by EDAX spectra. Finally a hybrid (geometric + internal field enhancement) model of electron emission from LAMIC thin films has been proposed.

Acknowledgements

The authors would like to thank the Deanship of Scientific Research, King Khalid University for their administrative and technical support.

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