INVESTIGATION ON LASER INTERACTION IN ANNEALING OF AMORPHOUS SILICON FILMS BY PULSED Nd$^{3+}$:YAG LASER

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INTRODUCTION
Semiconductors such as crystalline silicon play a major role in the application of MEMS devices and photovoltaic application, such as solar cells. Particularly, photovoltaic cells based on silicon are increasingly considered as one of the attractive renewable energy sources. However the resulting cost is high and overall size is limited. Hence an alternative cost-effective approach may be considered by employing laser annealing technique. Laser annealing technique is widely used to repair the defects caused during ion implantation in semiconductor processing [1]. This technique can also be extended to induce crystallization and modify amorphous silicon (a-Si) thin films to produce doped-poly-silicon films.

In this paper frequency tripled pulsed Nd$^{3+}$:YAG laser (355 nm) is made to interact on amorphous silicon thin films coated on the glass substrate. The surfaces of the treated samples are analyzed through Scanning Electron Microscope (SEM) and Raman spectroscopy to estimate the extent of crystallization and ablation. A one dimensional heat equation model is used to estimate the annealing and the ablation threshold in the laser treatment of a-Si films and to investigate the effect of parameters in annealing of a-Si films. The change in surface morphology in a-Si films due to the laser interaction has been correlated with the experimental and theoretical results to optimize the laser fluence for efficient annealing of a-Si for the production of polysilicon films.

THEORETICAL INVESTIGATION ON LASER ANNEALING OF SILICON FILMS
Laser annealing is a kinetic process where heating is used to change the microstructure through diffusion. When the laser is made to interact on the surface of a silicon film, it absorbs the energy. This absorbed photon energy makes the atom to vibrate and due to this heat starts to dissipate on to the surface. When the silicon film is irradiated with a laser with incident intensity $I$, according to Beer Lambert’s law, the variation of the intensity (transmitted intensity) with depth is given by $I = I_0 \times \exp(-ax)$. Where $I_0$ is the incident beam intensity ($W/m^2$), $I$ is the transmitted intensity ($W/m^2$), $x$ is the depth (m), $a$ is the absorption coefficient (1/m) and $R$ is the reflectivity of the surface. The optical energy ion absorbed by the silicon is converted into the thermal energy which is responsible for increase in a temperature of the film.

In this paper the heat flow on the surface of amorphous-silicon film is considered as one dimensional. The heat balance equation can be derived as,

$$\rho C_p \frac{\partial T}{\partial t} = a \times (1 - R) \times I_0 \exp(-ax) + k \frac{\partial^2 T}{\partial x^2}.$$  \hspace{1cm} \text{………...1}

Where $\rho$ is the density of the material (kg/m$^3$), $C_p$ is the specific heat capacity of the material (J/kgK), $a$ is the absorption of silicon, and $K$ is the thermal conductivity of the material (W/mK).

The above parabolic heat balance partial differential Eq.1 was solved using linear homogenous transformation system by considering initial and boundary conditions as $T(x,0)=0$; $T(x,t) = 0$ at $x = l$ and $K \neq 0$ [2]. The assumptions considered were: 1) The heat flow is one dimensional and it involves conduction only in one direction, i.e. along the depth; 2) Re-radiation of energy from the surface is negligible; 3) The thermal properties of the absorbing material are independent of the temperature; 4) The intensity and temperatures were calculated for single pulse duration $t = 19$ ns.

EXPERIMENTAL INVESTIGATION
The laser annealing was performed using a pulsed laser ablation equipment as shown in
The third harmonic of Nd³⁺:YAG laser (355 nm) was used with a 10 Hz repetition rate and a pulse width of 19 ns. The laser beam intensity profile was Gaussian and with a beam spot size of 6 mm. Amorphous-Si thin films (400 nm) coated on alkali-free glass wafers (total 0.5 mm thickness) were mounted on an X-Y stage. Laser beam was focused on the a-Si thin film with the focal length of 300 mm and irradiated spot size was approximately 1.5 mm in diameter.

When high intensity, short pulse-duration laser pulses are made to interact on the surface of the a-Si, the surface temperature reaches above or near to the melting point. As a result Si reaches the liquid temperature and starts getting crystallized as it cools. The crystallization of a-Si starts well above 900 °C and when the temperature exceeds above the melting point 1480 °C [3], it results in an ablation. The effect of the laser fluence value on the corresponding temperature of the irradiated zone was calculated using Eq. (1) and plotted as shown in Fig. 2. Subsequently, the threshold fluence values for the crystallization and the ablation processes were estimated.

The minimum temperature required for crystallization is 900 °C and the corresponding fluence value was estimated to be around 230 mJ/cm². The crystallization regime for a-Si films lies between 750°C and 1480 °C and the corresponding fluence values are estimated to be between 225mJ/cm² and 510 mJ/cm². When the films are treated with fluence value higher than the melting fluence (> 520 mJ/cm²) it results in ablation on the surface. The surface characteristics of a-Si thin films after the laser irradiation were investigated by the scanning electron microscopy technique (SEM) and Raman spectroscopy.

**B. Temperature and Recrystallization depth**

The amount heat incident on the a-Si thin film was estimated by using Eq. 1 for different laser fluence values. Figure 3 shows the temperature versus annealed depth for different laser fluence values.
When the laser beam with the fluence of 170 mJ/cm$^2$ was made to interact on the surface of the a-Si film the corresponding temperature incident on the surface was around 760°C and the temperature was decreased towards the depth of the coated a-Si. When the laser fluence of 280 mJ/cm$^2$ was made to interact on a-Si the corresponding incident temperature on the surface was estimated to be around 980 °C and the recrystallization depth was estimated to be around 0.1 µm depth. When the laser fluence was at 390 mJ/cm$^2$ the incident temperature was expected to be around 1170°C and the corresponding recrystallization depth was estimated to be around 400 nm. When the laser threshold fluence value was set to 690 mJ/cm$^2$ and at around 960 mJ/cm$^2$, the temperature was expected to reach above the melting point of a-Si which results in agglomeration and successive ablation of the a-Si films.

C. Surface Characterization of a-Si Films

Laser induced surface modification in silicon was studied through a scanning Electron microscope (SEM) and Raman spectroscopy to investigate the extent the crystallization and to estimate the ablation threshold. Figure 4 shows SEM photographs of a–Si films on glass substrates. Figure 4(a) shows the SEM photograph of the untreated amorphous silicon and no trace of grain or grain boundary was found at high magnification of 6000X. When the amorphous wafers are treated with a fluence of 170 mJ/cm$^2$, a minor modification on the surface was observed at 5000X magnification as shown in Fig. 4(b).

This represented that the laser fluence was not sufficient to start the crystallization but it was sufficient enough to impart a minor structural change. When the laser fluence was increased to 280 mJ/cm$^2$, the surface was modified as shown in Fig. 4(c). When the laser fluence of 390 mJ/cm$^2$ was made to interact on the surface of a-Si film, grain growth was observed as shown in Fig. 4(d). As compared to the lower fluence values, the grain growth was increased and uniformly distributed with the laser fluence value of around 390 mJ/cm$^2$. When a-Si films were treated with a higher fluence of around 690 mJ/cm$^2$, formation of spherical beads like structure which is termed to as agglomeration [4] was observed accompanied by an ablation as shown in Fig. 4(e). The diameter of the bubbles varied from a few micrometers to few tens of micrometer in size. The agglomeration created holes or spherical beads in the continuous a-Si films resulting into a serious damage. The agglomeration might have been due the boiling of molten Si. During the laser irradiation, outburst of heterogeneously nucleated vapor bubbles might have been promoted by the poor wetting property of a-Si film. When the a-Si films were treated with a fluence of 960 mJ/cm$^2$, a complete ablation was observed and the silicon film was completely removed in the irradiated region and the alkali free glass substrate was observed as shown in Fig. 4(f).

To investigate the extent of crystallinity the laser annealed samples were analyzed by using the Raman spectroscopy technique. Figure 5 shows the typical Raman spectra before and after laser treatment (with different laser fluence values). Crystalline silicon peak is also included to
Investigate the extent of crystallization. As shown in Fig. 5 there is a broadening of peak from 480-520 cm\(^{-1}\) for the untreated sample as compared to the other peaks treated at different laser fluence values. The SEM photographs and the Raman spectra illustrated above can be correlated with the irradiated sample temperature and crystallization. When the laser fluence of 170 mJ/cm\(^2\) was incident on the surface of a-Si the corresponding irradiated zone temperature was theoretically estimated to be around 760 °C which results in minor modification of the surface and this has been confirmed through the SEM photograph and the peak in the Raman spectra for the laser fluence of 170 mJ/cm\(^2\) is also slightly narrower than that of the untreated a-Si sample. When the laser fluence was set at 280 and 390 mJ/cm\(^2\) the corresponding temperature values were estimated to be 980 & 1170 °C, respectively, which is the crystallization regime and this has been confirmed through the SEM photograph and the Raman spectra where the peaks are narrow and lie within the range of standard crystalline peak as can be seen in Fig. 5. When the laser fluence was set at 690 mJ/cm\(^2\) and 960 mJ/cm\(^2\) the corresponding theoretical temperature values were estimated to be around 1800 and 2150°C, respectively, which were well above the melting point. This resulted in agglomeration and ablation of the a-Si film surfaces. This was also confirmed through the SEM photograph. Further, with the laser fluence value of 960 mJ/cm\(^2\), the temperature of the glass substrate was reached above the ductile to brittle transition temperature and crack formation on the surface of the glass was clearly observed as shown in Fig. 4(e). Based on the surface morphology and Raman spectroscopy studies, theoretical estimation of annealing and ablation regime were in good agreement with the experimental observations.

CONCLUSION
The influence of frequency tripled third harmonic pulsed Nd\(^{3+}\):YAG laser of 355nm in annealing of a-Si films has been investigated with different laser fluence values experimentally and theoretically. The films were analyzed using SEM and Raman spectroscopy. The amount of heat incident on the surface was been analyzed theoretically by solving one dimensional heat equation. The depth attained at different fluence was estimated. The theoretically estimated temperature of the irradiated region was highly matching with the results analyzed through SEM photographs and the Raman spectroscopy. The laser fluence for the efficient production polycrystalline silicon films is estimated to be between 300 mJ/cm\(^2\) and 500 mJ/cm\(^2\) for a thickness of 400 nm of a-Si films coated on glass substrates. The laser fluence for ablation threshold is estimated to be above 525mJ/cm\(^2\). This study can be extended to deposit an a-Si layer on a doped c-Si substrate by using a pulsed laser deposition (PLD) technique and subsequently annealing the same surface to produce a polysilicon surface. Subsequent doping of the polysilicon thin-film can allow fabrication of a heterojunction layer on Si wafer and photovoltaic devices.

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REFERENCES