Surface Properties of Aluminum-Silicon Alloy Irradiated by Picosecond Laser

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Abstract

This paper deals with the trial-fabrication processes of Aluminum-Silicon alloy realized by irradiation of picosecond laser pulses. Formation processes of morphology were analyzed from the time point of view. Quality of alloy was tested by both the electronic microscope and energy dispersive spectrometer (EDS). Parameters of pulses and ways of scanning have great effect on the appearance and distribution of compositions. Experiments illustrate that picosecond pulses are available in Al-Si alloy, more important, it could avoid the unwonted Al spiking which present elsewhere in the traditional high temperature sinter of Aluminum and Silicon.

1. Introduction

Ohm contact of Al-Si alloy is a critical process of solar cells for the quality of Al-Si contact affects both the electronic properties and reliability directly. Recent years, advanced manufactured technologies give rise to many new ways to realizing the fabrication of Al-Si alloy fast and efficiently, such as high temperature sinter in the protective ambience, fast thermal pulses alloying , and laser surface alloying and so on [1-3]. Low resistance, no rectifying effect, non electro migration are required for these processes as

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well as good conglutination, stability and erosion resistance. The broad used high temperature sinter shows disadvantages of aluminum spiking and pit erosion [4] in the interface of Al and Si for the non uniform cross diffusion, for which could lead to the failure of devices. And all of these drawbacks will be eliminated by the Al-Si alloy which fired by laser.

Laser processes get wide attention in decades for its advantages of precision, speediness and non contact. On the way to cost effective optoelectronic devices, ultrafast laser pulses play a decisive role especially in the manufactures of low cost per peak watt solar cells. At present, laser fired contacts (LFC) encourage photovoltaic industrial both in laboratory and production line [5]. 20.5% efficiency is obtained by using LFC in silicon solar cells [6]. In the fabrication of high efficiency solar cells, it is demanded that LFC should generate Ohm contact between Al and Si by firing through dielectric passivation layers, SiO₂ or SiNx commonly [7].

In our experiments, evaporated aluminum film was irradiated by the picosecond laser pulses for the Al-Si alloying. Single point irradiation and line scanning irradiation were used. Changes of surface morphology were analyzed in the time scale. Characteristics of the interaction between picosecond pulses and materials were discussed by the measurements of compositions. It is found that the irradiated Al-Si alloy are alternative comparing with the sinter alloy, but there are new disadvantages of ultrafast pulses irradiation, for instance, the over ablation and bombarded holes caused by the single point irradiation, which even damage the Al film and Si substrate. Whereas line scanning irradiation performs well in the formation of Al-Si cladding and prevents the Al spiking except for inducing the shrinkage cavities during the resolidification of liquid alloy.

2. Experimental

For the absorption of aluminum is almost constant from ultraviolet to near infrared, here the amplified passive mode lock picosecond laser system (home made, wavelength of $\lambda = 532nm$ by frequency doubling of 1064nm, pulse duration of $\tau = 30$ ps and a repetition rate of 1 kHz) with a computer controlled two axis galvanometer beam scanner were used. Picosecond laser is a good candidater in decreasing the costs of solar cells [8], therefore the investigation of picosecond laser induced contact alloy has great influence. The laser power delivered to the silicon was varied by a half-wave plate and polarizer assembly. The laser fluence $F$ is determined by $F = P/[f_{rep} \times S]$. Where $P$ is the laser power, and $f_{rep}$ is the repetition frequency of the picosecond laser, $S$ is laser spot area.

A photographic paper scanned by the picosecond laser was used to estimate the laser spot area. Measurement of the ablation sites using optical microscopy led to an elliptical shape and the following spot diameter dimensions: 90 $\mu m$ along the major axis and 60$\mu m$ along the minor axis. Aluminum film is evaporated on the surface of single crystal p-type Si (100) wafers with a resistivity of 2-5 $\Omega \cdot cm$. Thickness of Al film was 1 $\mu$m. Sample was placed inside a vacuum chamber that can be evacuated down to a base pressure of 1 Pa if necessary. Here single point irradiation which proceeded in 0.5Pa and line scanning which proceeded in air were performed by changing the irradiated time, scanning speed and translation step separately. Here the laser power for single point was 50mW, 60mW and 70mW, so laser fluence $F$ was from 1.18 to 1.65 $J/cm^2$. The experimental system is shown in Fig.1.
3. Results and Discussion

3.1 Single Point Irradiation

Surface morphology of single point pulses irradiation is shown in Fig. 2 (a), (b) and (c). Laser power was changing from 50mW to 70mW by the step of 10mW, while irradiated time kept constant of 3 second which means that each single point would receive 3000 pulses. Here we concluded that area of thermal effect region was expanding and ablation of center was worsening with the increasing of laser power. Several ablation area can be seen in the thermal effect region which includes that laser was working in multimode probably as shown in Fig. 2 (a), so the ablation of center mode was distinct compared with others and can be divided to three different parts: inner ablated region (Region 1); mid-eutectic region (Region 2); outside thermal effect region (Region 3), as illustrated in Fig. 2 (c).

Fig. 2. SEM micrograph of Al-Si alloy irradiated by pico-pulses, laser power of single point was from 50mW (a), 60mW (b) and 70mW (c) with 3000 pulses. Laser power of line scanning was 50mW with translation step of 50um and scanning velocity of 5mm/s (d), local amplified of line scanning (e) and cross-section micrograph (f). S1, S2, S3 and S4 indicated the position where EDS were performed.
When laser power exceeded 50mW, a clear elliptic ablated hole and the sputter crater with rough surface appeared in this region 1 (see in Fig.2 (b)). High thermal density of pulses made Al and Si melting and transformed to liquid Al-Si alloy instantly, concussion caused by pulses pushed liquid alloy aside. After irradiation, temperature grads of substrate made the surface cooling quickly, supplanted liquid alloy could not backtrack, so the bombarded deep holes were left [9]. Main composition of this region is Si for the melting Al was pushed aside as the elements contents of S2 shown in Fig.4. It is noted that the surface of these bombarded holes is quite rough which could reinforce the surface recombination. So the single point irradiation with high energy density will wreck substrate badly and even cause the deterioration of devices. In region 2, there are many particles which distributed closely and isolated by crack. Liquid Al-Si alloy pushed from inner ablated region was cooling and according to the theory of nonuniform nucleary, alloy particles sizing from 3 to 10nm were separated out. Elements contents is shown in the Fig.4 and Table1, 12% of Al atoms percentage are included in this region which implies the formation of Al-Si alloy as well as sinter around 570°C [10]. Region 3 is the thermal effect area which figures the deep color for the roasting of laser. Al film was not penetrated by the pulses.

Fig.3. shows the formation of dualistic alloy and surface morphology evolvement from the arrival of pulses to the completion of resolidification. Al film is melting and giving rise to the liquid/solid phase interface when the pulses arrive and irradiate the surface (b). Left Al film and part of Si is melting, phase interface is keep moving to the Si substrate, cross diffusion of Al and Si atoms makes the liquid alloy more uniform(c). Phase interface moves more and more slowly and reaches the maximum depth finally with the weakening of laser energy (d). Because of the temperature grad, liquid alloy begins resolidification from phase interface to the substrate surface. Si atoms resolved in the alloy separate out on the interface preferentially for Al and Si are not limitless mutual resolving system (e). Rest liquid alloy transforms to dual-alloy of Alx-Si1-x till the interface processes to the original surface (f). Si layer is doped to p+ type by Al atoms in the epitaxial layer and turns to Ohm contact finally.

Laser power and irradiated time should be controlled strictly in the single point irradiation. The compromise among completely melting, sufficient diffusion and melt should be went behind in order to preventing over ablation. Furthermore, the hardness and wear resistance of Al-Si alloy increase with increasing the Si content during the resolidification [11]. The maximum melting depth of the alloy zone can be diminished by reducing laser power or pulses numbers. Whatever, the over ablation and rough surface definitely have negative effects on the performance of photovoltaic devices as well as impose difficulties on the technical processes.

Fig.3. Sequential cross-section schematic illustration of mechanism for laser surface alloying from arrival of laser pulse to resolidification completion.
3.2 Line scanning irradiation

The surface micro-nano structures derive from line scanning irradiation are shown in Fig.2 (d), (e) and (f). Firstly, width of these structures is similarly to the dimension of pulses, which avoiding thermal effect to irrelevant region. So the line scanning irradiation can be used to the graphics Al-Si contacts which have strict require on the contact area. Secondly, surface of alloy with dispersed holes isn’t flat. Reason for this phenomenon is that liquid alloy layer caused by the irradiation will solidify and the upper and lower surfaces have different shrinking rate which caused by different cooling rate and surface tension, and shrinkage cavities show up on the surface without the complementary of liquid alloy and finally translate to holes, and this proves the phase transition during the irradiation and the presence of the Al-Si dualistic alloy [12].

Fig.4. EDS Spectrums of S1 and S2 of single point irradiation

Table 1. Elements content measurements of S1 and S2 irradiated by single point of laser pulses

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<th>Elements</th>
<th>Weight (%)</th>
<th>Atoms (%)</th>
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<tbody>
<tr>
<td></td>
<td>S1</td>
<td>S2</td>
</tr>
<tr>
<td>Al</td>
<td>11.72</td>
<td>3.61</td>
</tr>
<tr>
<td>Si</td>
<td>88.28</td>
<td>96.39</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
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Fig.5. EDS Spectrums of S3 and S4 of line scanning irradiation

Table 2. Elements content measurements of S3 and S4 irradiated by line scanning of laser pulses

<table>
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<tr>
<th>Elements</th>
<th>Weight (%)</th>
<th>Atoms (%)</th>
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<tr>
<td></td>
<td>S3</td>
<td>S4</td>
</tr>
<tr>
<td>C</td>
<td>33.47</td>
<td>23.60</td>
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Comparatively traditional sinter in the furnace will induce to the spiking for the non-uniform diffusion. Ultrafast pulses irradiation process rapidly which could escape from the Al spiking. Depth of thermal effect region meets exactly or even deeper than thickness of Al film, that means to say part of Si layer phase change else, and this depth can be diminished by reducing laser power or increasing scanning velocity. Nevertheless, as mentioned by reference [3], the most effective way is to displace the surface from the focal plane of the laser beam. With an increase in beam defocusing the depth of the melt zone decreases much faster and possesses a shallow profile which is suitable in the devices processes. Most important, transition between Al-Si alloy and Si substrate is glabrate and continuous which prevent the cross diffusion of Al to substrate, and this demonstrated by Fig.5 and Table 2 which indicate the gradually decreasing of Al content from surface to substrate. It’s worthy to mention that elements of carbon and oxygen are captured in the phase transition during the laser melting for samples were exposed to air and detected by EDS. In addition, in order to prevent Al film from oxidating, it is suggested that irradiation undergoing vacuum or the protective ambience with priority.

### 3. Conclusions

Al-Si alloy fired by picosecond laser pulses has been studied through surface and cross-section morphologies and EDS testing. It can be concluded that: (1) With regard to single point irradiation, laser power has great impact on the quality of dualistic alloy, balance between complete diffusion and over ablation is the key emphasis in our experiments. (2) EDS tests indicate the formation of Al-Si alloy qualitatively and we believe the components ratio can be controlled by changing laser power and scanning parameters. (3) Excellent quality of Al-Si alloy depends on laser parameters and ways of irradiation. Line scanning irradiation will stop Al diffusing into the Si substrate but at the risk of surface shrinkage cavity. Superiorities of laser irradiated fired Al-Si alloy are rapidity, accuracy and Al spiking free. The preliminary results just show the promising application of picosecond laser pulses irradiation in the approach of Al-Si alloy. High quality of Al-Si contact and parameterization analysis should be implementing in the subsequent work.

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References


