In-situ formation of magnesium silicide nanoparticles on the surface of the hydrogenated silicon films

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The magnesium silicide nanoparticles were formed on the surface of hydrogenated silicon thin films by thermal evaporation, annealing and hydrogen plasma treatment. The high reactivity of silicon and magnesium leads to the self-formation of magnesium silicide nanoparticles (NPs). The reaction is stimulated in-situ by the low pressure hydrogen plasma. The presence of Mg2Si NPs was confirmed by SEM and Raman spectroscopy. The photothermal deflection spectroscopy (PDS) shows the enhanced optical absorption in the near infrared spectrum. The diode structures with in-situ embedded Mg2Si NPs were characterized by the volt-ampere measurements in dark and under AM1.5 spectrum.

1. Introduction

The single solar cells on the base of hydrogenated silicon (Si:H) thin films exhibit the highest efficiency of solar energy conversion when the structure is mixed-phase, i.e. partly amorphous, partly microcrystalline. While the amorphous structure is characterized by higher absorption coefficient of light and thin films can be thinner, the microcrystalline structure has the character of crystalline silicon, the band gap is non-direct, the absorption coefficient is lower, and the final structure of solar cells has to be thicker. While the photo- and electro- luminescence of amorphous silicon is low but measurable, the microcrystalline structure does not exhibit those effects. One solution how to increase the absorption coefficient and the radiative recombination is to integrate nanocrystals with direct band gap to silicon layers. While the reactive deposition epitaxy (RDE) of silicide nanoparticles on silicon has been demonstrated [1,2], its large-scale application is limited. Plasma enhanced chemical vapor deposition (PECVD) is a convenient technique for large scale thin film deposition, but for the deposition of silicide nanoparticles it cannot be used, because it is impossible to transport the metal elements in a form of molecules of gases or vapors of some liquids into the vacuum reaction chambers. In our previous papers we have deposited silicide NPs in the diode structure ex-situ, i.e. with the interrupted vacuum process [3–6]. Recently we have introduced the PECVD in combination with the vacuum evaporation and plasma treatment (VE&PT) as a convenient nanoparticle formation process. In this paper we have improved the technology and realized all deposition processes in-situ.

2. Results and Discussion

2.1 Formation of the magnesium silicide nanoparticles

Our special vacuum chamber (see the Fig. 1, left) allows to alternate in-situ PECVD of Si:H thin films, vacuum evaporation from tungsten boat and hydrogen plasma treatment. For the deposition of
Si:H thin films we used 4.5 % of silane in hydrogen mixture (flow rates: hydrogen 50 sccm and silane 2.36 sccm), pressure of gasses during the deposition 30 Pa, deposition temperature 220 °C, RF power 18 W for glow discharge excitation at the industrial frequency 13.56 MHz (size of electrode: 62 × 62 mm², distance of electrodes: 32 mm). The thickness of evaporated Mg is controlled by the sensor. The details about the methods applied for the characterization of Si:H thin films with embedded nanoparticles are summarized in Ref. [7].

![Figure 1](image1.png)

**Fig. 1.** Special set up with the vacuum chamber for two *in situ* deposition processes: PECVD and vacuum evaporation from tungsten boat – the photo on the left and resulting structure of N-I-P diodes – picture on the right.

The surface morphology and NPs size and shape have been visualized in MAIA Scanning Electron Microscope (SEM), TESCAN. Fig. 2 shows that for the thicknesses 10 and 20 nm the surface of Mg monolayers is quite smooth, in the case of 30 nm clusters of Mg are already visible. Thus, higher Mg thickness leads to clustering. The surface reaction is strongly supported by hydrogen plasma treatment.

![Figure 2](image2.png)

**Fig. 2.** The SEM pictures of a-Si:H surface step by step covered by Mg of thicknesses 10, 20, 30 and 40 nm. The last picture shows the surface after the deposition of 40 nm Mg and 2 minutes hydrogen plasma treatment.
Raman scattering measurements were performed at room temperature by the Renishaw InVia Reflex Raman spectrometer using a CCD camera, the blue excitation wavelength of 442 nm in the backscattering geometry, see Fig. 3A. The normalized Raman spectra show the amorphous silicon band centered at 480 cm\(^{-1}\) and two Mg\(_{2}\)Si bands at 252 and 337 cm\(^{-1}\). These bands correspond to the optical phonon modes of Mg\(_{2}\)Si crystal [8]. The deposition of 5 nm Mg is not visible by SEM and cannot be detected by Raman spectroscopy. The optical absorption of Si:H thin films with and without embedded Mg\(_{2}\)Si NPs measured by photothermal deflection spectroscopy (PDS) is shown on Fig. 3B. The Mg\(_{2}\)Si NPs were created by evaporation of 10 nm Mg followed by hydrogen plasma treatment. The presence of NPs enhance the optical absorption in near infrared region indicating the presence of the localized states below the optical absorption edge of Si:H.

![Fig. 3](image-url)

**Fig. 3.** A) The normalized Raman spectra of a-Si:H with in-situ evaporated Mg layers and B) The optical absorption of Si:H thin films with and without embedded Mg\(_{2}\)Si NPs.

### 2.2 Diode characteristics

The diode structure is shown in Fig. 1 (right). The transparent substrate (Corning glass) was coated by the transparent conductive oxide (TCO) followed by about 30 nm thick phosphorus doped Si:H n-type layer, about 200 nm thick intrinsic Si:H layer with in-situ embedded NPs, 30 nm boron doped Si:H p-type layer and metal contact (Al).

The volt-ampere diode characteristics were measured by Keithley 6517A electrometer and AM1.5 solar simulator. The Fig. 4 and Table 1 show the similar open circuit voltage \(V_{oc}\) and the fill factor \(FF\) in diodes with and without embedded NPs. On the other hand, the decrease of the short circuit current \(I_{sc}\) is a negative effect that indicates the presence of undesirable recombination centers on the boundaries of NPs in silicon matrix. It remains an open question how to minimalize the recombination by in-situ annealing combined with the plasma treatment.
3. Conclusion

We have improved the method of the in-situ formation of the silicide nanoparticles (NPs) on hydrogenated silicon (Si:H) surface combining plasma enhanced chemical vapor deposition (PECVD), vacuum evaporation and hydrogen plasma treatment. The presence of magnesium silicide NPs was confirmed by SEM and Raman spectroscopy. The NPs embedded in Si:H thin film enhance the near infrared optical absorption by about order of magnitude. The Si:H based diodes with embedded magnesium silicide NPs show under AM1.5 illumination similar open circuit voltage and fill factor as diodes without NPs, but the defects induced by NPs deteriorate the short circuit current. We conclude that the PECVD deposition method in combination with vacuum evaporation and plasma treatment enhance possibilities of the in-situ deposition of Si:H thin films with embedded NPs. The vacuum process is perspective for large scale depositions with applications in photovoltaic and photonic.

Table I. The basic parameters of I-V characteristics, open circuit voltage $V_{oc}$, short circuit current $I_{sc}$, fill factor $FF$ and electrical power $P$ of diodes size 0.8 x 0.8 mm$^2$.

<table>
<thead>
<tr>
<th>$V_{oc}$ [V]</th>
<th>$I_{sc}$ [μA]</th>
<th>$FF$ [%]</th>
<th>$P$ [μW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No NPs</td>
<td>0.79</td>
<td>18</td>
<td>59</td>
</tr>
<tr>
<td>1x10 nm Mg</td>
<td>0.78</td>
<td>9</td>
<td>61</td>
</tr>
<tr>
<td>3x10 nm Mg</td>
<td>0.70</td>
<td>7.5</td>
<td>58</td>
</tr>
</tbody>
</table>

Fig. 4. The diode volt-ampere characteristics without (triangles) and with embedded Mg$_2$Si NPs (diamonds – one NPs monolayer, circles – three NPs monolayers). Full symbols - measured without illumination, empty symbols – measured under AM1.5 illumination.
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References