AGING EFFECTS ON THE NANOSTRUCTURE DEVICES

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The photoluminescence spectrum of the freshly photosynthesized porous silicon (PS) has been investigated. This measurement was repeated after three and six months for the same sample after storage under ambient condition (open air at room temperature). Photoluminescence (PL) measurements of the stored PS show different peak positions and intensity width as compared with the results of the fresh PS. A blue shift in PL peak positions with aging time was observed. PL relative intensity is strongly diminished after 6 months of aging. Dark I-V characteristics of Al/PS/n-Si/Al structure shows a behavior of PS/n-Si isotype heterojunction for fresh device and a MIS (metal-insulator-semiconductor) device due to contribution of Al/PS Schottky barrier after aging, essentially after 6 months.

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1. Introduction

Luminescent porous silicon is an important material because of its potential usage in futuristic optoelectronic devices. PS materials have been prepared by a variety of different methods such as photochemical, Photoelectro chemical [1-3] laser annealing [4] and anodization [5]. The electrical properties of photosynthesized PS layer in a PS/n-Si heterostructure has been studied by Ahmed et al.[6] they found that this structure presents a rectifying junction, confirming a formation of heterojunction. The authors also studied the photovoltaic properties of the Al/PS/n-Si double junction, and they found that the generated photo voltage is due to the contribution of the Al/PS Schottky junction and the PS/Si hetero junction [7]. In our experiments, we have fabricated porous silicon on n-Si wafer by photoelectrical chemical etching under zero bias conditions. The formation of this PS layer leads to the formation of a heterojunction between the PS and Si interface. Preliminary aspects for studying this heterojunction were characterized earlier [6,7]. The aim of this paper is to investigate the effect of atmospheric aging on the PL intensity, peak position as well as the I-V characteristic of this heterojunction. The PL spectra were analyzed by employing the quantum confinement model suggested by Canham et al.[8] to estimate the size of the silicon nanocrystallites as a function of aging time of PS.

2. Experimental procedure

Figure 1 shows a schematic diagram of the system used for the photochemical etching process. The system was built locally in our laboratories with non-complex and low-cost equipment. A commercially available n-type (111) oriented CZ silicon wafer of 3.5 Ω·cm was rinsed with acetone and ethanol (37%) HF acid. The immersed wafer was mounted on Teflon plates. In this photoelectron-chemical etching process, the applied current was 20 mA/cm². The light beam of the laser source of laser wave length 514 nm is focused on silicon wafer the etched area was 1.13 cm², the distance between the laser source and the wafer is about 15cm. Bubbles were observed during the etching process. The wafers were etched with 3000 s etching time, after
which they were rinsed with ethanol and dried with nitrogen gas. The porous layer was formed just on the side of the wafer illuminated by laser source.

![Fig. 1. Schematic diagram of the photochemical etching system.](image)

Room temperature PL was utilized to characterize the porous silicon layer. Since c-Si is not luminescent, the PL spectra were performed by exciting the photosynthesized PS layer with a He (Cd laser at a wavelength of 325 nm, with a low laser power density of nearly 10 mW/cm². The samples were characterized immediately after preparation, then the measurements were repeated after 3 months of atmospheric aging and then after 6 months. Electrical characteristics of PS/Si heterojunction were studied after deposition of 300 nm Al electrodes on both sides of the heterojunction by the vacuum resistive technique.

3. Results and discussion

Figure 2 shows the PL spectra of fresh and aged PS. The figure illustrates that the peak PL is at 2 eV (622 nm) for fresh PS, while the peak is shifted towards the right side (blue shift) to 2.13 eV (582 nm) after 3 months aging and to 2.43 eV (510 nm) after 6 months aging. This shift is attributed to the surface oxidation of PS during storage in the atmospheric ambient. The surface of luminescent PS is usually terminated by hydrogen or oxygen molecules[9]. The H-passivated surface is gradually replaced by an oxide surface, as PS is exposed to air.

It is also shown from the above Figure that the intensity is reduced and the Full Width at Half Maximum (FWHM) is increased after aging. The intensity is decreased after 3 months of aging to 60% from its value of the fresh sample, then to 14% after 6 months of aging. FWHM is increased from 470 meV for a fresh sample to 550 meV after 3 months of aging, then to 800 meV after 6 months of aging, as shown in Table 1. These drastic changes in relative intensity and FWHM after aging are attributed to the oxidation effect that causes nanocrystallite diminishing, and the carriers will be more confined, resulting in the diminishing of the nanocrystallites, which will decrease the photoluminescence. After 6 months of aging, PL disappears, since silicon oxide does not have strong PL characteristics.
Table 1. Related parameters extracted from PL spectrum.

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Relative peak PL intensity (%)</th>
<th>FWHM (meV)</th>
<th>Nanocrystallite mean size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>100</td>
<td>470</td>
<td>3</td>
</tr>
<tr>
<td>3 months aged</td>
<td>60</td>
<td>550</td>
<td>2.5</td>
</tr>
<tr>
<td>6 months aged</td>
<td>14</td>
<td>800</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 2. PL spectrum of PS before and after aging.

Depending on the position of the PL peak, the average size of nanocrystallites in the PS layer is calculated using the effective mass theory proposed by Canham et al.[8] The results are presented in Table 1. It is shown that the mean size of the nanocrystallites is decreased with the PL-peak blue shift. This decrease can be elucidated by the assumption that the emission is related to quantum size effects.

Dark J-V characteristics at room temperature of PS/n-Si heterojunction are presented in Fig. 3. Forward bias is achieved by applying the positive pole of the power supply on the Al side. The measurement of aged heterojunction was achieved by re-electroding the PS surface at a new point whenever it occurs, so as to include the effect of surface alterations after aging. The J-V curve of fresh heterojunction shown in this figure demonstrates a rectifying behavior due to the formation of an isotype heterojunction with low rectification factor (about 12 at 5 V), since PS is reported to be n-type when it is fabricated from n-type substrates.[10] The rectification factor is increased to 13, then 20 after the continual aging. This increase in rectification factor is attributed to the formation of a thin oxide layer between Al metal and Si. This interfacial layer introduces a MIS structure, which in turn leads to a decrease in reverse saturation current and hence increases the rectification factor. The contribution of Al/PS contact is not significant for fresh junctions, because the barrier height which is calculated from the semi-log I-V curve (not shown here) is 0.34 eV, with neglect of series resistance. The barrier height is raised to 0.35 eV, then to 0.39 eV after 3 and 6 months, respectively. This increase in barrier height is attributed to the formation of MIS structure at Al/PS contact by producing an oxide interfacial layer after aging. The increase in the
barrier corresponds to an increase in rectification characteristics with bit by bit lessening in the current values due to the increase in series resistance of the junction. The existence of the oxide layer and the increase of the PS resistivity (due to band widening) will result in an increase in series resistance, i.e., which is indicated by an increase in the slope of the forward current. Balagurov et al.[11] reported similar results for their Al/PS/c-Si heterojunction after aging, in which they attributed the improvement in the I-V characteristics of the aged samples to the substrate potential barrier.

From the results of PL and I-V, The oxide self-formation is deduced to be fair after 3 months of aging and considerably large after 6 months of aging.

4. Conclusions

Storage of PS under ambient condition (open air at room temperature) results in low photoluminescence due to formation of silicon oxide. The blue shift of PL is due to the decrease of nanocrystallites by the production of amorphous silicon oxide deep layer. The voidancy nature of the PS structure helps to increase the oxidation rate. Al/SiOx/PS MIS structure could be formed after aging, particularly after 6 months, and its influence is added to the fresh PS/Si isotype heterojunction. Aging can act to introduce feasible Al/SiOx/PS/Si/Al double junction structure. More investigations on current transport mechanisms of this double structure are under way.

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References

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