

## Surface Alkylation of Hydrogenated Amorphous Silicon by Grignard Reagent

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Surface alkylation of hydrogenated amorphous silicon thin films has been achieved by Grignard reaction. IR absorption spectra indicate the existence of C–H bonds that are due to covalent bonded decyl group on the surface of amorphous silicon. This modification can be a first step of novel organic–inorganic interface formation.

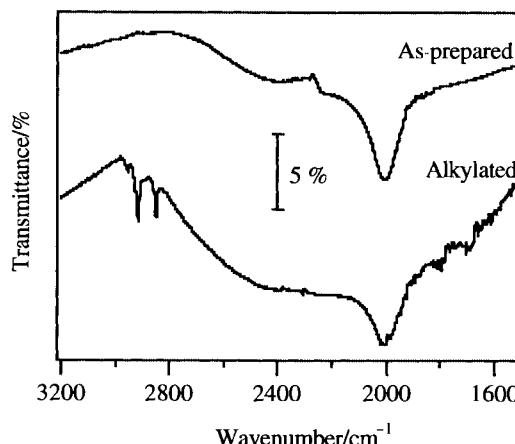
Hydrogenated amorphous silicon (a-Si:H) has been recognized as a useful semiconducting material for optical devices.<sup>1,2</sup> As the a-Si:H films are prepared by plasma enhanced chemical vapor deposition (PECVD), the films can be prepared on various kinds of structures, such as rough surface or patterned surface. This characteristic is similar to organic materials rather than conventional inorganic semiconductor materials. Thus, it can be thought that the a-Si:H is preferable material to form organic–inorganic interfaces in which crystalline silicon cannot be epitaxially grown. However, the resistance of the interface is thought to be higher than conventional inorganic–inorganic interfaces. It is because inorganic and organic materials are not covalent bonded with each other. Thus, there is a boundary layer at the interface with high energy gap. In addition, the interfaces could not be thermally annealed to form alloys like metal–semiconductor interfaces. This interface energy gap will be a problem when devices become in smaller scales. However, if the inorganic–organic materials are covalent bonded with each other, the interface resistance must be reduced because the carriers do not have to tunnel the interface boundary layer.

In the present work, we have investigated the surface alkylation of a-Si:H using Grignard reagents at room temperature. Although similar surface modifications have been observed in the case of porous silicon (PS),<sup>3</sup> the surface of the PS is not smooth. The modification on smooth surface will be required for organic–inorganic interface device preparation. The research can be recognized as a first step of covalent bonded low resistive organic–inorganic interface formation.

a-Si:H thin films with thickness of 0.5 μm were prepared by PECVD. The silicon source gas was hydrogen-diluted SiH<sub>4</sub> (10%) at a feed rate of 50 sccm. Rf power, substrate temperature and deposition pressure were 30 W, 370 °C and 133 Pa, respectively. These conditions were determined to reduce internal stress of a-Si:H films to avoid the peeling off of the films. We used Si wafer (100) for substrate to make it possible to monitor the reaction by IR spectra.

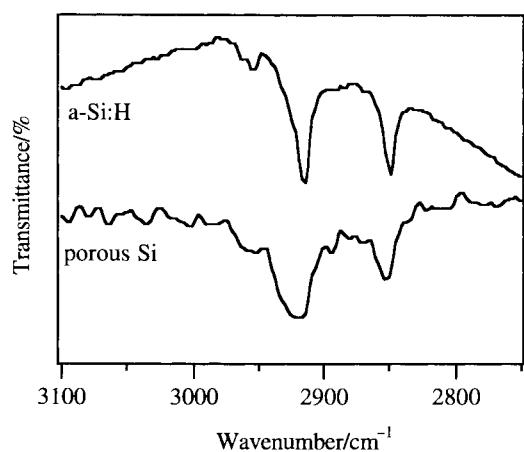
The surface modification reaction was carried out by the condition described as follows. Magnesium (3.0 g, 0.12 mol) is put in a dried 300-mL round flask. Then, a solution of 36.6 g of 1-bromodecane (0.15 mol) in 80 mL of dried diethyl ether is added dropwise with stirring. Thus a solution of decylmagnesium bromide of 1.2 M concentration is synthesized and used in the following procedure. Alkylation of the a-Si:H samples was

carried out by dipping a-Si:H sample (12 mm × 12 mm) in decylmagnesium bromide ether solution for 3 h at room temperature with stirring. Then, the samples were taken out and quenched in 1 M HCl subsequently. After quenching, the samples were washed with a good amount of ether, water, and acetone.<sup>3</sup> We have chosen decyl group with a relatively large molecular size as the alkyl group in order to limit the penetration of the Grignard reagent into bulk a-Si:H



**Figure 1.** IR absorption spectra of as-prepared a-Si:H and surface alkylated a-Si:H by Grignard reagent (1.2 M).

In Figure 1, IR spectra of a prepared a-Si:H and an a-Si:H sample after the treatment with decylmagnesium bromide ether solution with concentration of 1.2 M are shown. The spectrum of the prepared sample shows peak of Si–H stretching mode at 2000 cm<sup>-1</sup>. In the spectrum after alkylation, three peaks of C–H stretching mode are observed at the wavenumber of 2850, 2915 and 2950 cm<sup>-1</sup>. The intensity of the C–H peaks are significantly lower than in the case of alkylated PS.<sup>3</sup> In addition, the C–Si peak that can be a direct evidence of surface derivatization has not been observed. This result is due to the smooth surface of a-Si:H that has smaller net area of the surface than PS. In addition, amount of Si–C bonds is 1/21 of C–H bonds that show weak peaks. Thus, the peak of Si–C bond becomes undetectable. However, the authors think the surface has been substituted by alkyl group. The C–H peak-intensity has not been affected by rinsing with hydrofluoric acid or various organic solvents in ultrasonic cleaner, or by annealing at 100 °C in vacuum (less than 10<sup>-3</sup> Pa). 1-Bromodecane or Grignard reagent that is another candidate for the C–H peaks cannot exist after such treatments. Thus, the C–H peaks can be an evidence of surface alkyl bond formation, although the Si–C peaks could not be observed clearly. Further modification of alkyl group, such as oxidation of alkyl to carboxy or amide formation with



**Figure 2.** Detailed IR absorption spectra of alkylated a-Si:H and alkylated porous Si.

amines will be described elsewhere.

In the present work, we have studied the effects of Si structure to C-H bonding properties in alkyl (decyl) group. In Figure 2, detailed IR spectra of alkylated a-Si:H and alkylated PS are shown. As shown in Figure 2, the peak position and peak width are different from each other. The C-H peaks observed in PS are at 2852, 2920 and 2960  $\text{cm}^{-1}$  that are at higher wavenumber than in a-Si:H. In addition, the width of the peaks are two or three times larger than those observed in alkylated a-Si:H. The authors think the difference is caused by different structure and chemical composition between a-Si:H and PS. The alkyl groups are thought to be bonded to a-Si:H or PS as terminator of dangling bond (DB). We have reported that the difference in electron paramagnetic resonance (EPR) spectra corresponds to difference in DB structure directly.<sup>4</sup> In the a-Si:H, the EPR spectra indicate broad signal of DB with width of

5–7 G.<sup>5</sup> The EPR spectra of the DB in the PS prepared under the condition in the present work show larger and more anisotropic distribution than a-Si:H.<sup>6</sup> The peak width of the DB in the PS structure is more than 8 G. This result indicates that the variety of Si structure around a DB is larger in the PS than the a-Si:H. It may be the cause of the larger width of C-H peaks in alkylated PS. In addition, we have to point out the effects of oxygen atoms exist in PS. As the oxygen has large electron negativity, it can cause the decrease in bond length of C-H that changes the peak position of C-H peak to higher wavenumber. The magnitude of the effect of oxygen atoms to individual C-H bond is different. It can also be a cause of larger peak width in PS. It can be concluded that these two kinds of difference induce the different peak width and position of the C-H in alkyl group.

As an another kind of merit of this surface modification, we want to mention the termination of dangling bond defects at the surface by formation of Si-C bonds. It has been reported that surface layer of the a-Si:H has higher DB density than inside bulk layer. Surface alkylation of a-Si:H by the method in the present work will reduce the DB in this surface defective layer. The performance of the organic–inorganic interface device also improved by surface DB termination.

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