Conductive Atomic Force Microscopy Measurements of Localized over Dark Current along Pyramidal Ridge Lines of Intrinsic Hydrogenated Amorphous Silicon Layer on Textured Crystalline

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Localized over dark current of a hydrogenated amorphous silicon (a-Si:H) layer deposited on p-type crystalline silicon with a pyramidal texture was measured by conductive atomic force microscope. The current followed the ridge lines of the pyramidal a-Si:H texture, and a large over dark current corresponded to a low open circuit voltage ($V_{oc}$). The current path has two possible phenomena: variable film thickness, local crystallization, and a-Si:H degradation. By modifying the textural structure, the current path of the a-Si:H layer deposited on crystalline silicon with a pyramidal texture can be reduced; thereby the possibility of preserving the $V_{oc}$ of hetero-junction with intrinsic thin layer solar cells could be suggested. [doi:10.2320/matertrans.M2016354]

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Hetero-junction with intrinsic thin layer (HIT) solar cells are unique high-efficiency silicon solar cells developed from amorphous silicon (a-Si:H) and crystalline silicon (c-Si) solar cell technologies.1-3) The high open circuit voltage ($V_{oc}$) of HIT solar cells is primarily derived from the effective passivation of defects on the c-Si surface, which is coated with high-quality a-Si:H. Fujiwara and Kondo reported that the performance of HIT solar cells strongly depends on the interface of a-Si:H and c-Si.4) Schaper et al. developed high-quality a-Si:H on c-Si by plasma-enhanced chemical vapor deposition (PE–CVD) at a deposition temperature of 225°C. Their cell demonstrated high passivation ability in quasi-steady-state photo conductance assays.5) The c-Si surface of HIT solar cells is textured to increase the light-trapping effect and consequently the density of the short circuit current ($J_{sc}$). The texture size has been frequently investigated as a means of improving light trapping and lifetime.6,7) However, $V_{oc}$ of solar cells with a textured substrate is lower than that of cells with a flat substrate. The reduced $V_{oc}$ has been attributed to degradation of the intrinsic amorphous hydrogenated silicon (i-a-Si:H) layer, which works as a passivation layer.8) Film deposition on flat and textured surfaces differs primarily by the multiple deposition conditions engendered by the pyramidal textures.9) Particularly in the textured case, epitaxial growth and/or mixed phase probably occurs on a nanoscopically uneven surface.9) Fesquet reported that the carrier lifetime increased in proportion to the size of the pyramidal texture, and that $V_{oc}$ could be increased by reducing the sharpness of the pyramids as well as the sub-micron pyramid density using isotropic etching.9) In the pyramid valleys, the film is not conformal, and epitaxial growth occurs.9) Of equal morphological importance but much less investigated are the ridge lines of the pyramidal texture. We surmised that the pyramid ridges, in addition to the valleys, are detrimental to conformal film. Therefore, investigation of the microscopic electronic properties of a-Si:H along the ridge lines of textured c-Si is necessary.

Conductive atomic force microscope (C-AFM) is an effective tool for microscale investigation of electronic characteristics, but few researches of thin film measurements using this technique have been reported.10,11) In the present study, dark current characteristics and the map of i-a-Si:H on p-type textured crystalline silicon were measured by C-AFM in order to evaluate the i-a-Si:H layer on textured c-Si at the microscale.

The samples consist of amorphous silicon deposited on a pyramidal textured p-type crystalline silicon substrate (thickness = 0.28 mm). Prior to deposition, the textured substrates were rinsed by four processes: acetone with supersonic vibration for 5 min, Semico Clean 23 (Furuuchi Chemical) for 5 min, Frontier Cleaner A01 (Kanto Chemical) for 3 min, and 47% solution of hydrofluoric acid for 5 min. After each process, the substrates were rinsed with super pure water for 1 min. The surface of a pyramidal textured p-type crystalline silicon substrate was modified to smooth the sharpness or angle of inclination of ridge lines by using Tetramethylammonium hydroxide, TMAH (Tokyo Chemical Industry Co., Ltd.) as etching solution. The density of TMAH was 1% and, the temperature is 353 K for 25 s.

Intrinsic a-Si:H films were prepared by the radio frequency (RF) PE–CVD method. Under typical conditions, the substrate temperature and RF (13.56 MHz) power density were fixed at approximately 543 K and 44 mW/cm², respectively. The base pressure was approximately 7 × 10^{-5} Pa. The source gas was pure silane flowing at 5.0 sccm. The total gas pressure of deposition was fixed at 53 Pa.

C-AFM measurements (height and current mappings) of the a-Si:H surface were obtained by a scanning probe microscope (Hitachi High-Tech Science, SP400 and Nanonavi 2). Figure 1 is a schematic of the C-AFM setup. A silicon-based cantilever coated with rhodium films (SI–DF3 R) was used for the measurements. During current mapping, a negative
bias voltage (relative to the cantilever) was applied to the substrate to prevent anodic oxidation coating of the silicon substrate. AFM/current imaging was performed in sampling intelligent scan (SIS-AFM) mode which is a kind of static mode conducted with force curve measurement of each sampling point. In this scan mode, the probe approaches the sample only while acquiring data. SIS enables accurate measurements of surface shapes with high aspect ratio and minimizes damage to both cantilevers and samples. All measurements were performed in air at atmospheric pressure. The surface morphology of textured substrate modified with etching of TMAH was obtained by Scanning Electron Microscope (SEM). The cross sectional surface morphology of heterojunction was observed by Transmission Electron Microscope (TEM).

Figures 2(a) and (b) show the height and current mapping, respectively, of a flat c-Si substrate. Equivalent mappings of a-Si:H deposited on a flat substrate with a bias voltage of $-1$ V are shown in Figs. 2 (c) and (d). A comparison of Figs. 2 (b) and (d) shows that the a-Si:H layer decreases the current. An a-Si:H layer of 10 nm thickness deposited on a flat substrate with a bias voltage of $-1$ V behaved as a passivation layer, establishing uniform current across the composite structure.

Figures 3(a) and (b) show the height and current mapping, respectively, of a bare textured c-Si substrate. The bias voltage was $-1$ V. The current is distributed as shown in Fig. 3(b), but no correspondence between height and current is evident. This result indicates that the current path is independent of the textural structure of the naked c-Si substrate.

The height mapping, current mapping, and overlapped image of a-Si:H on a textured c-Si substrate is shown in Fig. 4. The a-Si:H layer was 10 nm thick and a $-1$ V bias voltage was applied to the substrate. Figure 4 (a) demonstrates the pyramidal nature of the texture, which was sized at several micrometers. Clearly, the current distribution follows the pyramidal texture (Fig. 4 (b) and (c)). Specifically, the current follows a line-path along the ridge lines of the pyramid, and over dark current is observed on some of the pyramid faces. This current path was considered to be driven by the a-Si:H at the ridge lines, because it did not develop on the bare c-Si substrate (Fig. 3(a) and (b)). Figure 5 plots the I–V characteristic along the ridges and at the centers of faces where the current was small. The I–V characteristics markedly differ between the ridges and the face centers.

To elucidate the reason for this difference, we obtained enlarged C-AFM images. Figures 6(a)–(c) show the detailed height, current, and overlapped mappings along a ridge line of the pyramidal texture. The current distribution along the ridge line appears as an assembly of small grains (Fig. 6 (c)).

In order to investigate the cause of over dark current, we checked the relation between the film thickness of the amorphous layer and the measured current on a flat substrate using C-AFM. The result of this investigation showed that the thicker the deposited film, the lower the over dark current. Figure 7 shows the cross sectional TEM image of a typical hetero-junction sample of this study. The thickness of a-Si:H in the ridges and in other parts are uniform, no difference in thickness was observed. Although the thickness is uniform,
the over dark current was measured due to other reasons.

Figure 8 (a) shows the SEM image of modified textured crystalline silicon substrate etching with TMAH. The new plane direction was formed around the ridge lines of the pyramidal and was surrounded by (111) plane directions. It seems that it is (311) plane direction. Figures 8 (a) and (b) show the height and current mapping, respectively, of a bare textured c-Si substrate. The bias voltage was $-1\, \text{V}$. The characteristic over dark current path was not observed in Fig. 8 (c) (etching with TMAH), but was observed in Figs. 4 (b), (c) and Figs. 6 (b), (c) (without etching). This study showed the relation of the sharpness of the ridge lines of the pyramids (before and after etching) with over dark current; on the other hand, Fesquet has reported the relation with $V_{oc}$. Hence, there appears to be there a relation between over dark current and $V_{oc}$.

The large over dark current may arise from two phenomena. The first possibility is local crystallization of the i-a-Si:H layer. The I–V characteristics of microcrystalline film differ from those of a-Si:H film, and establish larger currents at the same bias voltage.\(^{11}\) No microcrystalline and epitaxial crystal silicon growth occurs at the bases of the pyramids.\(^9\) A similar crystallization pattern could occur in the present study. Therefore, the observed current grain in Fig. 3(c) may reflect crystallization along the ridge lines. The second one is the degradation of a-Si:H under ion bombardment. Controlled bombardment with ion atoms enhances the degradation of a-Si:H based surface passivation of c-Si surfaces. The decreased level of surface passivation is independent of ion kinetic energy (within the range 7–70 eV).\(^{12}\) Under our deposi-
The over dark current was not observed around the ridge lines modified with etching of TMAH in Fig. 8 (b), (c). According to this result, the influence of textured structure on the current measured by C-AFM was observed. Moreover, this study shows the corresponding tendency with Fesquet. The open circuit voltage of the HIT solar cell also could be decreased along the ridge lines.

Using C-AFM, we investigated the microscopic electronic properties of a-Si:H deposited on pyramidal c-Si substrate. Over dark current paths were only established along the sharp ridge lines of the a-Si:H pyramids without TMAH etching. Possible reasons for this phenomenon were suggested as local crystallization and degradation by ion bombardment in the PE–CVD process. We conclude that the observed current path could reduce the $V_{oc}$ and that the texture could be modified to increase the $V_{oc}$. C-AFM is effective for evaluating the microscale electronic properties of a-Si:H on textured c-Si.

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REFERENCES