論文の内容の要旨

論文題目　Local Characterization on Solar Cells by Photoassisted Kelvin Probe Force Microscopy
　　　　　（光ケルビンプローブフォース顕微鏡による太陽電池の局所的物性評価）

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　　A wide variety of solar cells are recently researched and brought to the market. To realize the high-performance solar cells, the "evaluation" of the solar cells is crucial process because the information obtained by the evaluation is beneficial for the fabrication process and leads to the improvement of the conversion efficiency. The evaluation of the solar cells is classified into three phases: the modules, the cells and the materials. In this study, we focus attention on the evaluation of the materials used in the solar cells, for which the method of the microscopic evaluation is needed. On the other hand, scanning probe microscopy (SPM) is powerful tool for evaluating sample surface, and is used in many different scientific disciplines including surface science, materials science, surface chemistry, electrochemistry, biology, metrology, etc. There are many kinds of microscopy such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), magnetic force microscopy (MFM), Kelvin probe force microscopy (KFM) and so on. Such a SPM technique, where the interactive force between the tip and sample surface are used, enables us to obtain various significant information of the sample surface with high spatial resolution. The study aims to develop the novel evaluation methods using Kelvin probe force microscopy (KFM), which is a kind of SPM and characterize the solar cells of the multicrystalline silicon and $CuInSe_2$ thin film materials by those methods to improve the solar cell efficiency.

　　The KFM is based on atomic force microscopy (AFM), and allows us to obtain potential information of sample surface with high spatial resolution by detecting an electrostatic force between a tip and a sample. On the other hand, we originally proposed Photoassisted Kelvin probe force microscopy (P-KFM), which consists of KFM and laser system, and it enables us to obtain photovoltage as well as potential information with high spatial resolution. For accurate photovoltage measurements in our P-KFM, we make all kinds of efforts. For instance, we use a piezoresistive cantilever suited for photovoltage measurements and adopt the new feedback method of potential determination. Furthermore, we have developed the methods by P-KFM for obtaining diffusion length, lifetime and mobility of minority carriers.

　　First, we adopted these P-KFM methods to multicrystalline silicon solar cells to investigate the local characteristics on these materials. Multicrystalline silicon solar cells exceed

single-crystal ones in production volume mainly because of their great advantage in terms of fabrication cost, but are inferior to single-crystal silicon solar cells in terms of conversion efficiency. The influence of grains and their boundaries (GBs) in such multicrystalline materials is a possible cause of the low conversion efficiency.

In photovoltage measurements, we performed photovoltage mapping around the GB on a certain area including GB. Consequently, we confirmed photovoltage drop around the GB and photovoltage difference between the different grains. We also found that this site dependence of photovoltage can be well explained from the intrinsic potential distribution obtained in the dark condition, where the potential became high at the GB. When the intrinsic potential for electrons is low or high, the electron is attracted or repulsed, respectively, and therefore the photogenerated electrons accumulate in the low potential region rather than the high potential region. Since the photovoltage depends on the number of electrons accumulating in the surface n-type layer, the photovoltage in the high potential region should be lower than that in the low potential region, which is very consistent with the experimental results obtained by our P-KFM method.

In our method for evaluating minority carrier diffusion length, the basic principle used to evaluate the diffusion length is same as that used in the conventional SPV method, where laser light at various wavelengths was used to illuminate the sample surface and the photovoltage as a function of the wavelength of the illuminating laser light was measured to estimate the diffusion length. To investigate the diffusion length around the GB, we mapped the diffusion length distribution. As a result, we observed a reduction of the diffusion length in the vicinity of the GB. Additionally, differences in the diffusion lengths between the grains existed even when the influence of lateral diffusion was considered.

In minority carrier lifetime measurements by P-KFM, a sample surface is illuminated by a modulated light and the minority carrier lifetime is extracted from a temporally averaged photovoltage at various modulation frequencies. This method enables us to evaluate a bulk recombination lifetime without independently of surface recombination lifetime without any surface passivation process as well as to investigate a spatial distribution of at high spatial resolution. From the lifetime measurements, we found the lifetime decreasing in the vicinity of the GB in the multicrystalline silicon solar cell material. These results of photovoltage, diffusion length and lifetime measurements indicate that the GB degrades the solar cell performance by acting as a carrier recombination site.

By Einstein relationship, the minority carrier mobility was also numerically obtained from the diffusion coefficient, which was derived from the diffusion length and lifetime values. The mobility difference was observed between the grains, and this result indicates that the crystal quality differs between the grains.

Second, we have applied the P-KFM method to $CuInSe_2$ (CIS) materials such as $Cu(InGa)Se_2$ [CIGS] and $Cu(InAl)Se_2$ [CIAS] for purpose of the microscopic characterization of local properties around the GBs in these materials. Thin film solar cells based on CIS materials have attracted a growing interest in recent years because of their prospective high performance. The band gap of CIS materials is variable by the addition of Ga and Al. Most of the CIS materials used in the solar cells present multicrystalline structures, but the behavior of their grain boundaries GBs to the solar cell is not fully understood yet. In this study, we used CIGS and CIAS materials. The CIGS material is widely used for solar cell devices and very recently, CIAS materials have also been regarded as another candidate owing to wide tunability of their band gap.

We investigated the surface potential distribution of the as-grown CIGS and CIAS films in the dark condition. As a result, we observed the abrupt drops of the potential at the GBs on both CIGS and CIAS films. One possible cause of this potential distribution is a change in the material composition near the GBs due to the segregation within the single grains. The observed potential distribution implies that the photogenerated electrons in the CIGS and CIAS layers tend to accumulate near the GBs rather than to stay on the grains.

To investigate the photovoltaic properties in the solar cells on CIGS or CIAS materials, we measured the surface potentials in the dark condition again and under the light illumination by P-KFM. The surface potentials of both samples under the dark condition showed the similar features to those on the as-grown surfaces of CIGS and CIAS films, where the abrupt drops of the potential clearly appeared near the GBs. This fact suggests that the surface potential distribution on the solar cell structures were still dominated by the underlying CIGS or CIAS layers even after forming some additional layers. The observed potential distribution means that the photogenerated electrons will gather near the GBs as mentioned above. Actually, photovoltage enhancement at GBs was observed. This behavior of the GB was quite different from that in the multicrystalline Si materials where the photovoltage, the diffusion length and the lifetime of the minority carriers were apparently degraded near the GBs. Therefore, we can expect that the GBs in CIS materials do not act as a carrier recombination center and this inactiveness of the GBs is a big advantage for the solar cell application.

To characterize the GBs in more detail, we investigated the dependence of the potential drop at GBs on a ratio of Ga to (In+Ga) in the CIGS layer and defined the potential drop around the GB as the built-in potential. As a result, we found that the built-in potential monotonically decreases as an increase of Ga ratio. Moreover, we performed photovoltage mapping on two CIGS solar cells at the Ga ratio of 0.2 and 0.5, and compared the photovoltage distributions between two samples. The results indicate that the photovoltage distribution becomes flat as an increase of Ga ratio. These results of the dependence of the built-in potential and photovoltage

distribution on Ga ratio imply that the material composition becomes uniform inside the single grain of CIGS layer. We also found that the whole photovoltage generated in the sample at the Ga ratio of 0.5 is higer than that in the sample at the Ga ratio of 0.2. This increase in photovoltage is simply attributable to the difference in the band gap of the CIGS material.

We also performed scanning tunneling spectroscopy (STS) measurement, which uses a STM to probe the local density of electronic states (LDOS) and band gap of surfaces and materials on surfaces at the atomic scale. We investigated the difference of the band gap of CIGS at between the grain and the GB. As a result, we found that the band gap at the GB is 0.4 eV higher than that at the grain. This result indicates that the material composition differs between the grain and the GB. Furthermore, we consider that the carrier recombination at the GB is less likely to occur, owing to the band diagram on CIGS layer, where the electrons is easy to accumulate and the holes are repulsed at the GB.