Depth profile analysis of solar cells by Secondary Neutral Mass Spectrometry using conducting mesh

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Abstract

Depth profile analysis of solar cells was performed by Secondary Neutral Mass Spectrometry (SNMS), which is a suitable technique for quantitative analysis of the composition of layered structures. However, in the case of insulating samples or samples prepared on non-conductive substrates (e.g. microslide, oxidized silicon wafer) the charge accumulation on the sample surface due to ion beam bombardment can cause a serious problem by destroying the resolution of depth profile. The high frequency (HF) mode of electron-gas SNMS seems to be a good solution for this problem. Another method to prevent the charge accumulation on a sample surface can be a conducting mesh (e.g. copper, stainless steel) placed on the surface. Using one of the two methods mentioned above can help us to get rid of the charging effect, i.e. to neutralize the surface charge during measurements. But in the case of solar cell analysis these two methods should be applied simultaneously during depth profiling. The experimental results performed on p-i-n:Si (p-type/intrinsic/n-type) diodes have proved that SNMS measurement in HF operation mode combined with a mesh is very efficient in the determination of doping levels of phosphorus and boron with good depth resolution, even in the case of 500–600 nm thick samples.

1. Introduction

In the last few decades continuously growing energy consumption has provided solid support for the development of renewable energy technologies. Among these technologies the most promising one is solar energy conversion. The silicon thin film solar cell is a preferable choice for the large-scale production of low-cost solar modules for numerous reasons: (i) an abundance of cheap raw material; (ii) the non-toxic component of the technology; (iii) shorter energy payback time; and (iv) low temperature technology [1]. In low-power applications, amorphous silicon (a-Si) based systems are typically used and the commercially available modules provide relatively low stable efficiency (5–7%). From the early 1990s onwards, a new material, the microcrystalline silicon (μ-Si) system appeared in laboratory scale research. This material can be deposited by a technology similar to the amorphous one, but offers major advantages: (i) 1.1 eV bandgap (1.7 eV of the a-Si) allows the utilization of the near infrared spectral range of the incident solar light; and (ii) a lower degradation rate, i.e. higher stable efficiency [2]. A new and promising way for photovoltaic application of μ-Si is the so-called “micromorph tandem” structure, which is a serial combination of an amorphous and a microcrystalline cell [3,4]. The development and implementation of this technology into an industrial manufacturing line may result in the reduction of specific processing costs and increased efficiency. On the other hand, not only production, but also analysis of the produced layers is important in order to increase the efficiency of energy conversion.

One of the most effective methods for characterizing the layered structure of a solar cell is the depth profile analysis. Secondary Neutral Mass Spectrometry (SNMS) has proved to be an excellent technique for the quantitative analysis of the composition of layered structures, especially when high depth resolution and sensitivity is required [5,6]. In the HF operation mode, when a square-wave type high frequency voltage is applied to the sample instead of a constant dc voltage [7,8], the SNMS in most cases is a suitable technique for the analysis of electrically insulating samples. According to the phase of the driving potential, the ion bombardment process is periodically interrupted at low voltage parts of the square-wave. During interruption times the electrons of the plasma reach the specimen and this process makes possible the neutralization of the positive charge.

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accumulated on the surface during ion bombardment periods. The frequency and duty cycle of the applied square-wave voltage are chosen so that the surface potential should remain negligibly small during measurements.

However, in some types of insulating samples or in case of a large sputtered area, the surface charge cannot be neutralized exclusively by applying the HF method during depth profile analysis. In these cases, in addition to the HF method, an electrically conducting mesh placed on the sample in tight contact with the surface can help to eliminate the charge accumulation problem [9,10]. A precise measurement of depth distribution requires a decrease, or even an avoidance, of a charge accumulation on the sample surface. For this purpose, in analyses of insulating samples, the high frequency sputtering mode combined with an electrically conductive mesh on the sample surface must be used. In the following we show the results of measurements obtained with and without a mesh on the amorphous p-i-n:Si diode of solar cell samples. The intrinsic layer of a p-i-n amorphous silicon photovoltaic cell behaves as an insulating layer. According to our experience, while the charge accumulation in the intrinsic insulating layer without a mesh makes it impossible to determine the small amount of doping elements with good depth resolution, the HF operation mode combined with a mesh was very efficient in determining the phosphorus and boron dopants with good depth resolution, even in the case of 500–600 nm thick samples.

2. Experimental details

In our experiments an INA-X type SNMS equipment (SPECS, Berlin) was used for depth profile analysis of amorphous p-i-n:Si diodes of solar cell samples. The surface bombardment and post-ionization of sputtered neutral particles were made at low pressure by Electron Cyclotron Wave Resonance (ECWR) argon plasma. The SNMS was operated in high frequency mode. A 350 V sputtering potential at 100 kHz frequency with 50% duty cycle was applied on the sample. The investigated area was confined within a circle 8 mm in diameter by a Ta mask. The lateral homogeneity of the ion bombardment, which is the lateral ion energy distribution at the same time, was examined by investigation of the sputtered crater and the surface roughness. These data were used as input parameters and the theoretical depth vs. concentration distribution of the defined element was calculated. This method allowed us to predict the sputtering process and revealed the real depth distribution of elements in a layer.

3. Results and discussion

With the employed experimental arrangement our purpose was to achieve the best possible depth resolution in a half micrometer depth. Because the detection of small concentration elements requires surface sputtering in a relatively large area, a tantalum mask with an inner diameter of 8 mm makes it possible to achieve the desired sensitivity. As it has already been mentioned above, the shape of crater indicates the distribution of the bombarding ion current density. In order to achieve the required sputtering parameters, the bottom surface of the crater profile must be as flat as possible. As can be seen in Fig. 1a, the crater profile was concave in the case of HF mode measurements, which makes analyzing depth profile complicated. In this case the depth profile of the sample is very poor, and the boron distribution in 500 nm depth could be determined with a pure depth resolution (Fig. 1b). As a result, the originally prepared 40 nm thick boron layer was smeared up to 300 nm. Thus the crater shape plays the main role in the distribution determination of the dopants in the layered structure. We can conclude that the inhomogeneous lateral distribution of ion current was induced by charge accumulation on the central part of the sputtered area due to the considerable difference of electrical conductivities between the sample and Ta mask. Because of the large sputtered area, the HF mode operation itself was not a satisfactory method for neutralizing the sample surface in the central part of the sputtered region.

In order to avoid the charge accumulation, in the second experiment a copper mesh screen was used on the sample surface with a 350 × 350 µm² opening size and 500 µm periodicity. Fig. 2

![Fig. 1. The crater shape (a) and depth profile (b) of a p-i-n:Si diode measured without a metal mesh. The open circles show the calculated concentration values of Si.](image-url)
shows the arrangement of the sample holder equipped with the mesh.

The effect of this electrically conductive copper mesh placed on the sample surface during sputtering together with the HF method proved to be excellent. While the crater shape and the depth resolution were poor without a mesh (Fig. 1), their quality was remarkably improved with a metal mesh (Fig. 3). Fig. 3a shows the shape of the crater after sputtering. It can be seen that the bottom of the crater was close to the ideal square-shape, in contrast to the previous one presented in Fig. 1a. As the sample surface under the grid was shadowed and the material was not sputtered, spikes were created. Thus from the sputtering point of view, the grid was considered a mask. However, we did not detect the elements of the grid constituents. Their presence in the plasma did not influence the results. To verify our experimental results, we calculated the theoretical depth distribution of Si, based on the measured surface roughness and crater shape. We found that the calculated data correspond precisely to the measured values, as shown on experimental curves by open circles in Figs. 1b and 3b. In the experiment when the sputtering was made through a mesh, the interface between the Si layer and the substrate was very sharp, in contrast to the other arrangement, which also means that the crater shape plays a dominant role in the determination of depth resolution.

4. Conclusion

In this paper we discussed how charge accumulation developed on the surface of an insulating sample due to sputtering could be avoided by using a conducting mesh. The HF method of SNMS combined with a conducting grid on the surface of the sample proved to be an excellent arrangement to perform depth profiling of dielectric/insulating samples with the same quality that was achieved in the case of conducting samples. This method was successfully applied to the analysis of p-i-n:Si diodes, and the results confirmed that measurements with a conductive mesh were more effective in determining the doping level of phosphorus and boron in 500–600 nm depth than measurements done without a mesh. Although the measurements were produced on amorphous Si samples, the method can be applied to μ-Si, as well. To the best of our knowledge, this was the first measurement where the whole p-i-n diode structure of a solar cell was investigated by SNMS.

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References