JJMIE

Volume 4, Number 1, Jan. 2010
ISSN 1995-6665
Pages 151 - 154

Jordan Journal of Mechanical and Industrial Engineering

New Method for Quality Evaluation of Mc-Si Wafers Implied in the Fabrication of Photovoltaic Cells

Mohamed FATHI *, Ahmed CHIKOUCHE

UDES, Solar Equipments Development Unit

Route National N11, Bouismaïl, BP 386, 42415 Tipaza, ALGERIA

Abstract

We have developed a new method for quality evaluation of mc-Si wafers implied in the fabrication of photovoltaic cells. This method is based on the exploitation of the variation of the sheet resistance ($\Delta R_\square$) of chemically etched wafers. We have presented specific classification connecting directly $\Delta R_\square$ bands to the crystalline defect types and densities. These results are in good accordance to physically observed defect density and grain boundaries repartition. Previously, with special process experimentation, we have shown that the best sensitivity to crystalline extended defects in mc-Si material is supported by the "Secco Etch" chemical solution. This chemical is very sensitive to crystalline defects and was applied to the development of our new characterization method of mc-Si wafers.

Keywords: Multicrystalline Silicon Wafers; Crystalline Defect Density; Four Probes Technique; Chemical Delineation; Photovoltaic.

1. Introduction

Crystalline extended defects of a mc-Si wafer can affect various aspects of photovoltaic cells manufacturing, from device performance to production yield [1]. Indeed, the presence of crystalline defects and impurities leads to losses of energetic efficiency in the photovoltaic cells [2]. Many investigations have shown that the final electrical properties of these devices are directly correlated with the crystalline defect density in the bulk material [3, 4]. This study has two main objectives. The first one was the selection of a more sensitive chemical agent in order to localize, identify and calculate the crystalline defect density. The second one was the implementation of a new technique for the identification and mapping of crystalline defect density on the whole mc-Si wafer area, all in one step. The mc-Si ingots analyzed here have been produced in our laboratory by the Heat Exchanger Method (HEM) [5].The Observation with an optical or a scanning electron microscope (SEM) of the crystalline extended defects (dislocations, stacking faults, twins, precipitates, etc...), requires a chemical etch called delineation step [6]. Several chemical solutions such as, Dash, Sirtl, Secco, Yang, Wright etc.., are commonly used for silicon defect delineation. However, the defect delineation process depends on silicon surface crystallographic orientation and topography [7]. The first used etch was Dash Etch which reveals dislocations in all crystallographic orientations but necessitates very long etching times [8]. Sirtl reveals dislocations only on (111) surfaces [9]. Secco etches defects in all orientations and gives circular defect pits [10]. Yang solution gives good defect delineation in all orientations and its etch pit shapes (triangular, quadratic, etc...) are function of surface orientation [11, 12]. Wright etch [13] is widely used in the semiconductor failure analysis field and especially for high temperature induced defect analysis; it is effective in all orientations but its composition is more complex than Secco and Yang. Furthermore, Wright etch is less sensitive to dislocations generated during crystal growth than Secco and Yang solutions [12, 13].

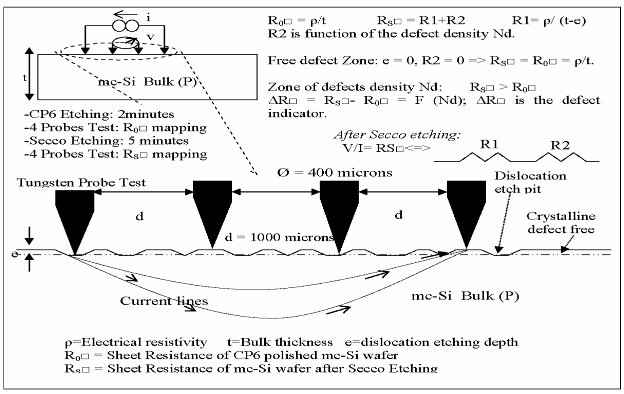

Figure 1. Principle of crystalline defects detection by sheet resistance variation.

We have chosen to develop our defect analysis process with the Secco and Yang etches, because our first interest was studying dislocations induced by HEM mc-Si growth, and also variable grain crystallographic orientations on

Corresponding author. Email: dr_fathimohamed@yahoo.fr

mc-Si material. Both etching solutions are sensitive to all kind of crystalline defects and also to all crystallographic orientations. The specificity of mc-Si HEM material has necessitated a special adjustment of Yang and Secco etching process parameters (time, agitation, temperature, etc…).

The principle of the developed technique for the mapping of crystalline defects is based on the exploitation of the sheet resistance variation in the delineated zones of crystalline defects. The delineation process consists of the action of a selective etching agent which will attack more quickly the crystalline defected zones than the other zones. This is due to the fact that in defected regions, the disturbance of the crystal lattice causes weak atomic bonds. The decoration of defect will take place only on the crystal grains levels; the zones of grain boundaries will be uniformly and more quickly etched than the grain surface because the atomics bonds are too weak there. Thus, the measurement of sheet resistance on the etched area should indicate a variation compared to the initial value obtained before application of the delineation solution on the wafer. A more defected area should lead to a higher increase in sheet resistance. In order to obtain a significant increase of sheet resistance, it is important to cause major perforations at the defect sites. Therefore, longer etching times than used for SEM defect inspection are necessary.

This new concept for crystalline defect mapping would provide time reduction and easy automation for defects analysis. It would be applied for the study of the defect density variation with the wafer position along the ingot. It would also be useful for the control of defects induced by each processing step during photovoltaic device manufacturing.

The sheet resistance measurement technique and crystalline defects delineation are both well established techniques in semiconductor characterization field. However, the combination of these two techniques for mapping crystalline defects is a new and useful approach. Indeed, in comparison to other techniques such as automated light scattering [14] or Sopori scanning machine [15], our technique is more economic in terms of time and cost. It is also more adapted for a first diagnostic to make a qualitative and fast study of the defect

2. Experimental

We have used P-type Boron doped mc-Si wafers of 10 x 10 cm2 in dimension and of about 1 Ω.cm in electrical resistivity. They were sawed from ingots grown by the Heat Exchanger Method (HEM). In order to remove the sawing process damage, we have begun by thinning and polishing these wafers. During this step, we have used an acidic polishing solution (known as "CP4 Etch") made by mixing nitric acid (HNO_3), acetic acid (CH_3COOH) and hydrofluoric acid (HF) with respectively 50%, 30% and 20% concentrations. After 6 min of etching, we rinsed thoroughly the mc-Si wafers with deionized water and dried them under a nitrogen gun. In order to test the Secco and Yang solutions, samples were cut from a polished mc-Si wafer. Mainly, the etching time and the agitation mode were varied. Before each delineation trial, the samples were immersed in diluted HF (10%) solution for 30 seconds in order to remove the native silicon dioxide (SiO_2) and then rinsed in deionized water. The Secco [10] formulation is HF/potassium bichromate ($K_2Cr_2O_7$)/H_2O, obtained by mixing 2 parts of HF with 1 part of $K_2Cr_2O_7$/H_2O at (0.15Moles) or (44grams of $K_2Cr_2O_7$ in 1litre of H_2O). The Yang [11] formulation is HF/chromic acid (CrO_3)/H_2O, obtained by mixing 1 part of HF with 1 part of CrO_3/H_2O at (1.5Moles) or (150grams of CrO_3 in 1litre of H_2O). After the Secco or Yang etching process the samples were immediately rinsed in deionized water and nitrogen dried. Subsequently, SEM observation and other analysis have been performed.

For the development and study of defect density mapping technique, we have used a mc-Si wafer previously polished by "CP4 Etch", with a final thickness of about 325µm (±5µm). By using an automated four probes tester, we have measured the sheet resistance at 25 different positions which were well defined and regularly distributed across the wafer surface. Stamp marks were applied on the probe tester carrier as a reference to allow positioning of the wafer exactly at the same place during the next measurement step (following the crystalline defects etching). Once the sheet resistance mapping of the polished mc-Si wafer was over, we carried out a desoxidation of the wafer with HF (10%) during 30 seconds followed by water rinsing. Then, we proceeded to the delineation of the crystalline defects. For this step, we have chosen to apply "Secco Etch" during 5 minutes. The etched mc-Si wafer by Secco solution was then precisely positioned under the 4 probe tester, and the sheet resistance was measured again at the same 25 initially selected positions. Thereafter, we calculate and plot the sheet resistance variation ($\Delta R_\square$) mapping. This result and its correlation is presented and discussed below. Figure 1 is a typical representation of this developed technique.

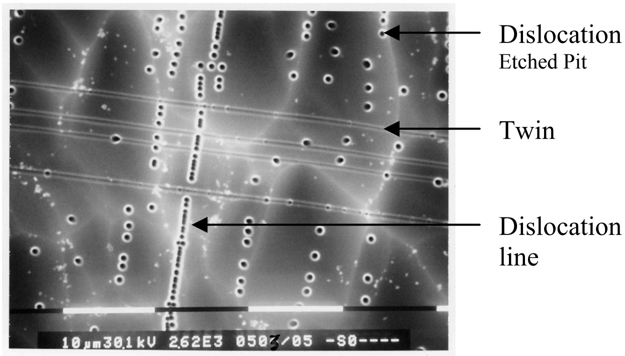

Figure 2. Secco defects delineation on mc-Si

3. Results and Discussion

The results of Yang and Secco delineation studies confirm the revelation of crystalline defects for an immersion time from 1 to 2 minutes, by clearly delineating dislocations, twins, grain boundaries and dislocation lines. We observed that dislocation pits etched with the Yang solution have mainly triangular or quadratic forms, whereas the dislocation pits are circular when using the Secco solution. Figure 2 is an illustration of Secco defect delineation process under the optimized conditions.

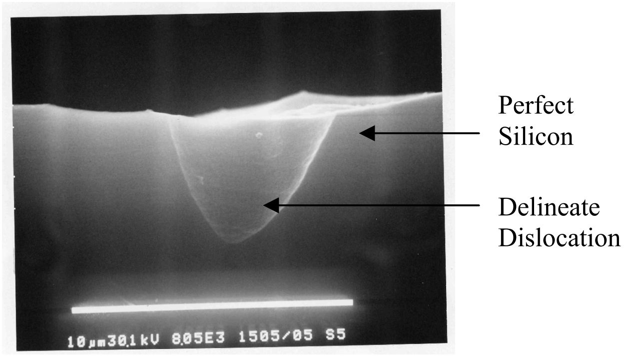

Figure 3. Cross section of dislocation delineated by Secco Etch for 5 minutes

In order to compare the action of dislocation localization between Secco and Yang solutions, we carried out a Secco revelation on a sample previously revealed with Yang Etch and vice-versa. The aim was to enable us to make a choice between Secco and Yang Etches for the calculation of the maximum density of defects. These tests showed that the action of Secco is higher than Yang's and lead us to choose Secco for the calculation and mapping of dislocation density. The profile of etched dislocation pits revealed by this solution is shown on Figure 3. The dipping time of the Secco delineation process was fixed at 5 minutes for the following defect mapping study. Such dipping time removes 5 µm of the dislocation zone as shown by the SEM micrograph of Figure 3. This fine knowledge and control of crystalline defect decoration by "Secco Etch" on mc-Si wafers were directly applied to the development of defect detection by the sheet resistance variation technique.

Once the sheet resistance mapping of a polished mc-Si wafer (10x10 cm2) was completed, we submitted the wafer to a Secco etch during 5 minutes. We chose this revelation time in order to strongly mark the defected zones and thus obtain an appreciable variation of sheet resistance. The mc-Si wafer revealed in this way was then precisely placed under the 4 probes tester, and measurement of the sheet resistance was carried out at the initially selected positions. We plotted the mapping of sheet resistance variation (ΔR□) on the 25 selected points of the mc-Si wafer. The Figure 4 shows the layout obtained for ΔR□. The next step was the superposition of the physical image of decorated mc-Si wafer with that of the ΔR□ mapping. In order to accomplish this, we have taken a digitalized photo of the whole Secco etched wafer surface, scaled it, and finally successfully superposed it to ΔR□ mapping. The Figure 4 illustrates this original result. The SEM analysis of these results allowed us to make the first classification for ΔR□ bands according to the revealed crystalline defect type and average dislocation density. This classification is summarized on Table 1.

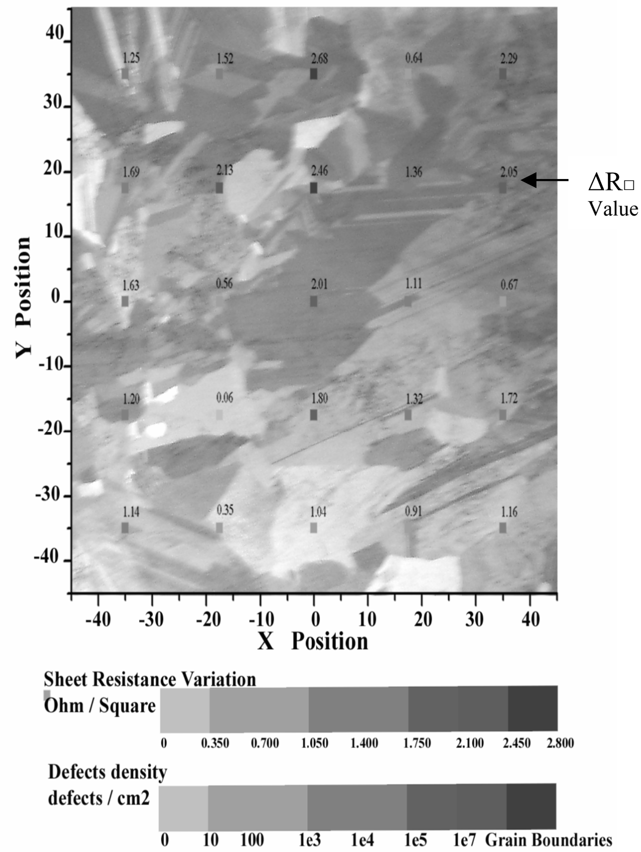

Figure 4. Superposition of the physical image of the defects area with ΔR□ mapping

Finally, by using this interesting correlation between sheet resistance variation (ΔR□) and defect density, we have plotted the mapping of the average defects density mapping on a whole mc-Si wafer (see Figure 5). These mapped values are in good agreements with those obtained from SEM analysis by counting etch pits. Sheet resistance mapping with the four probe technique has less resolution (it is about 3 mm) than the automated optical microscopy mapping technique. However, it gives sufficient information about defect distribution for photovoltaic device manufacturing. We can say that our developed technique is a good tool for making a quick diagnostic of the average dislocation density repartition in the mc-Si wafer and grown ingots.

Table 1. Classification of defects types according to sheet resistance variation bands

ΔR□ BANDS[Ω/□]	IDENTIFICATION AND DENSITY OF DEFECTS (Nd).
ΔR□ ≤ 0.35	Clean area without any defects
0.35≤ ΔR□ ≤ 0,7	Area with very low dislocations density $10cm^{-2} < Nd < 100cm^{-2}$
0.7≤ ΔR□ ≤ 1,050	Area of low dislocations density $100cm^{-2} < Nd < 10^3cm^{-2}$
1,050 ≤ΔR□ ≤ 1.400	Area of medium dislocations density $10^3cm^{-2} < Nd < 10^4cm^{-2}$
1.400 ≤ΔR□ ≤ 1,750	Area of high dislocations density $10^4cm^{-2} < Nd < 10^5cm^{-2}$
1.750 ≤ΔR□ ≤ 2.100	Area of very high dislocations density. $10^5cm^{-2} < Nd < 10^7cm^{-2}$
2.100 ≤ΔR□ ≤ 2.450	Twins area and / or grain boundaries
2.450 ≤ΔR□ ≤ 2.800	Area of grain Boundaries

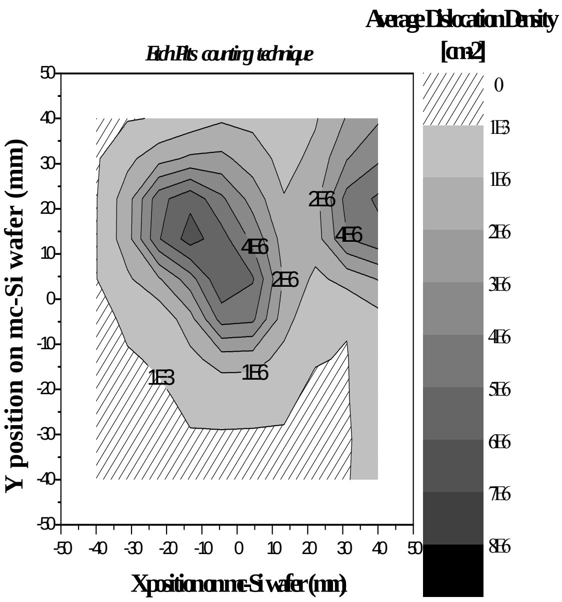

Figure 5. Plotting of the average defects density mapping by using sheet resistance technique.

Conclusion

By specific experimentations on mc-Si wafers, we have optimized chemical delineation process of crystalline extended defects. It appeared that Secco Etch is the more sensitive solution to crystalline defects. Therefore, it was applied for calculation and mapping of dislocation density. We have demonstrated the feasibility of a new technique for detection and mapping of the crystalline defects on a whole mc-Si wafer area. This method is based on the exploitation of the variation of the sheet resistance (ΔR□) of Secco delineated defective zones. We have presented the first classification connecting directly ΔR□ bands to crystalline defect types and densities. These results are in good accordance to physically observed defects density and grain boundaries repartition.

References

[1] M. Karilahti, PhD Thesis, Helsinki University of Technology, February 2003

[2] D.H. Macdonald, PhD Thesis, the Australian National University, May 2001

[3] M. Spiegel, PhD Thesis, Konstanz University of Physics, October 1998

[4] E.B. Yakimov, J. Phys. III France, December 1997, 2293-2307

[5] V.G. Popov, Quantum Electronics & Optoelectronics, Semiconductor Physics, Vol.3 , No. 4, 2000, 479-488

[6] M.S. Klukarni, J. Libbert, S. Keltner, J.Electrochem. Vol. 149 No.2, G153-G165 , 2002.

[7] Semiconductor Materials and Process Technology Handbook, Edited by Gary E., McGuire, 1988

[8] W.C. Dash, J. Appl.Phys. 27, 1956, 1193

[9] E. Sirtl, A.Z. Adler, Metallkd. 52 , 1961, 529

[10] [F.Secco d'Aragona, J. Electrochem. Vol. 119, 1972, 948.

[11] K.H. Yang, J. Electrochem. Vol. 131, 1984, 1140

[12] K.H. Yang, Semiconductor Processing, ASTM STP 850, Dinesh C. Gupta, Ed., American Society for Testing and Materials, 1984

[13] W.M. Jenkins, J. Electrochem. Vol. 124, 1979, 479

[14] B.L Sopori, J .Electrochem. Vol. 135 , 1988, 2601-2607

[15] B.L. Sopori, R. Murphy, C. Marshall, 23rd IEEE Photovoltaic Specialists Conference, 1993, 190