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A new detection technique of crystalline defects by sheet resistance measurement on multicrystalline silicon wafers

Mohamed Fathi and Djoudi Bouhafs

UDTS, 2 Bd Frantz Fanon, BP 399 Alger-Gare, Algiers, Algeria

E-mail: dr_fathimohamed@yahoo.fr

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Abstract

The mapping of crystalline defect density on the whole area of a 10 × 10 cm^2 multicrystalline silicon (mc-Si) wafer is a long and difficult task if one uses the conventional techniques of chemical delineation followed by optical or electron microscopy. We have demonstrated the feasibility of a new procedure which proved less time consuming and well adapted to mc-Si wafer quality test automation. This new method is based on the measurement of the sheet resistance variation resulting from defective zones etched by a chemical which is sensitive to crystalline defects. Previously, with special process experimentation, we have shown that the best sensitivity to extended crystalline defects in mc-Si material is supported by 'Secco etch'. This chemical sensitivity to crystalline defects was applied to the development of a new technique for dislocation and defect density mapping. Using an automated four-probe test bench, we have extracted the sheet resistance variation mapping of an mc-Si wafer before and after Secco etching. We have successfully correlated this mapping to the physical image of crystalline defect density and grain boundaries distribution on the whole mc-Si wafer.

1. Introduction

Crystalline extended defects of an mc-Si wafer can affect various aspects of photovoltaic 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 the crystalline defect density on the whole mc-Si wafer area, all in one step. The mc-Si ingots analysed here have been produced in our laboratory by the heat exchanger method (HEM) [5].

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 the 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 the Dash etch which reveals dislocations in all crystallographic orientations but necessitates very long etching times [8]. Sirtl reveals dislocations only on (1 1 1) surfaces [9]. Secco etches defect in all orientations and give circular defect pits [10]. The Yang solution gives good defect delineation in all orientations and its etch pit shapes (triangular, quadratic, etc are a function of surface orientation [11, 12]. The 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, the Wright etch is less sensitive to dislocations generated during crystal growth than Secco and Yang solutions [12, 13].

Table 1. Yang and Secco parameter effects on etched dislocation pits of mc-Si HEM samples.

Sample reference	Solution	Dipping time	Pit geometry	Pit width (μm)	Decorating effect
Y0	Yang	30 s	Pits too small	0.5	Weak
Y1	Yang	1 min	Triangular	1	Good
Y2	Yang	2 min	Triangular	2	Good
Y2u	Yang	2 min + ultrasonic agitation	Over etching	4–6 irregular	Medium
Y3	Yang	3 min	Triangular	3.8	Good
Y4	Yang	4 min	Over etching	Irregular	Medium
Y5	Yang	5 min	Over etching	Irregular	Bad
S0	Secco	30 s	Pits too small	0.6	Weak
S1	Secco	1 min	Circular	1.1	Good
S2	Secco	2 min	Circular	2.3	Good
S2u	Secco	2 min + ultrasonic agitation	Circular	4	Good
S3	Secco	3 min	Circular	3.3	Good
S4	Secco	4 min	Circular	4.6	Good
S5	Secco	5 min	Circular	5	Medium

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 the mc-Si material. Both etching solutions are sensitive to all kinds of crystalline defects and also to all crystallographic orientations. The specificity of the 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 in the crystal grains levels; the zones of grain boundaries will be uniformly and more quickly etched than the grain surface because the atomic bonds are too weak there [2]. Thus, the measurement of the sheet resistance on the etched area should indicate a variation compared to the initial value obtained before the application of the delineation solution on the wafer. A more defected area should lead to a higher increase in the sheet resistance. In order to obtain a significant increase of the 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 the 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 details

We have used p-type boron-doped mc-Si wafers of $10 \times 10\,\mathrm{cm}^2$ in dimension and of about 1 Ω cm in electrical resistivity. They were sawed from ingots grown by the 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 the ‘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, 16 samples were cut from a polished mc-Si wafer. These samples were referenced as shown in table 1. Mainly, the etching time and the agitation mode were varied. Before each delineation trial, the samples were immersed in a diluted HF (10%) solution for 30 s in order to remove the native silicon dioxide (SiO_2) and then rinsed in deionized water. The Secco [7, 10] formulation is HF/potassium bichromate (K_2Cr_2O7)/H_2O, obtained by mixing two parts of HF with one part of $K_2Cr_2O_7$/H_2O at 0.15 mol or 44 g of $K_2Cr_2O_7$ in 1 L of H_2O. The Yang [7, 11] formulation is HF/chromic acid (CrO_3)/H_2O, obtained by mixing one part of HF with one part of CrO_3/H_2O at 1.5 mol or 150 g of CrO_3 in 1 L 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 analyses have been performed.

For the development and study of the defect density mapping technique, we have used an mc-Si wafer previously polished by ‘CP4 etch’, with a final thickness of about 325 μm (± 5 μm). By using an automated four-probe 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

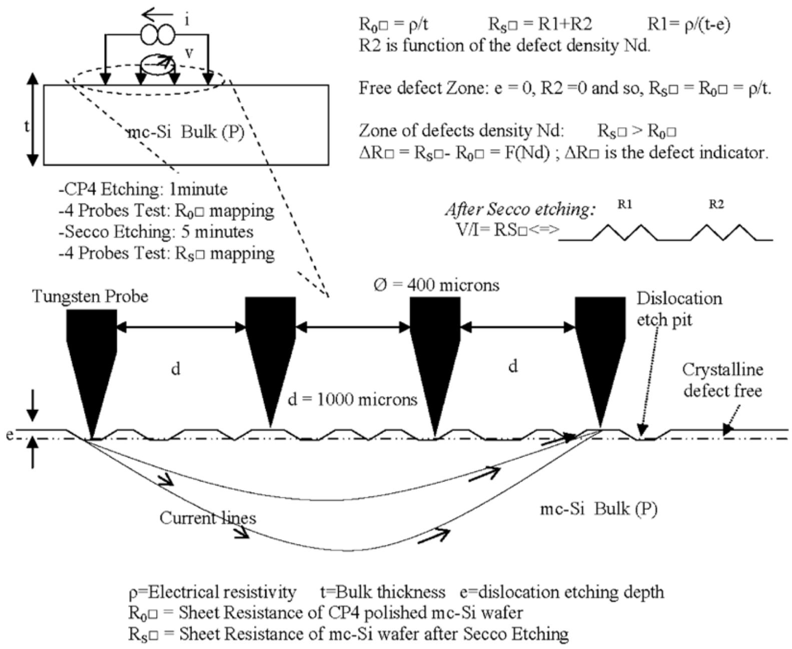

Figure 1. Principle of crystalline defect detection by sheet resistance variation.

mapping of the polished mc-Si wafer was over, we carried out a desoxidation of the wafer with HF (10%) during 30 s followed by water rinsing. Then, we proceeded to the delineation of the crystalline defects. For this step, we have chosen to apply the 'Secco etch' during 5 min. The etched mc-Si wafer by the Secco solution was then precisely positioned under the four-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 are presented and discussed below. Figure 1 is a typical representation of this developed technique.

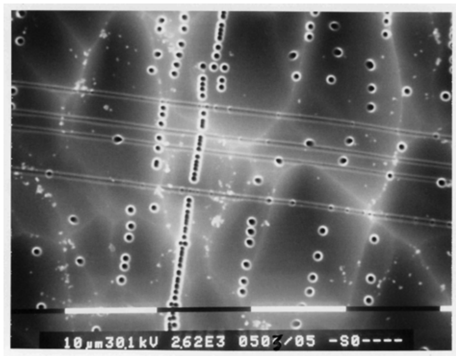

Figure 2. Secco defect delineation on mc-Si.

3. Results and discussion

Table 1 illustrates the etching parameters that were varied for Yang and Secco delineation studies. In this table, we also summarized our observations and remarks. These results confirm the revelation of crystalline defects with the Yang solution. For this solution, an immersion time from 1 to 2 min without ultrasonic agitation gives the best results by clearly delineating dislocations, twins, grain boundaries and dislocation lines. The same study leads us to choose for the Secco solution, a dipping time of 1 min under ultrasonic agitation. We noted that in the Secco etching process, the ultrasonic agitation was very useful for the elimination of gas bubble artefacts and gave the cleanest surfaces for the SEM analysis. We showed that dislocation pits etched with the Yang solution have mainly triangular or quadratic shapes, whereas the dislocation pits are circular when using the Secco solution. Figures 2 and 3 are good illustrations of Secco and Yang defect delineation processes under the optimized conditions given above. We have frequently noted that the zones close to the grain boundaries contain a strong population of defects. This is a foreseeable phenomenon since on the grain boundary level

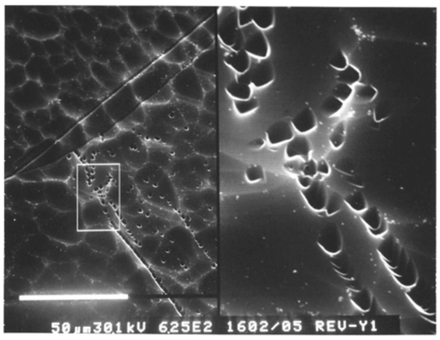

Figure 3. Yang defect delineation on mc-Si.

there is a change of crystallographic orientation leading to a stressed zone which reaches its thermodynamic equilibrium by the emission of dislocations [16].

In order to compare the action of dislocation localization between Secco and Yang solutions, we carried out a Secco

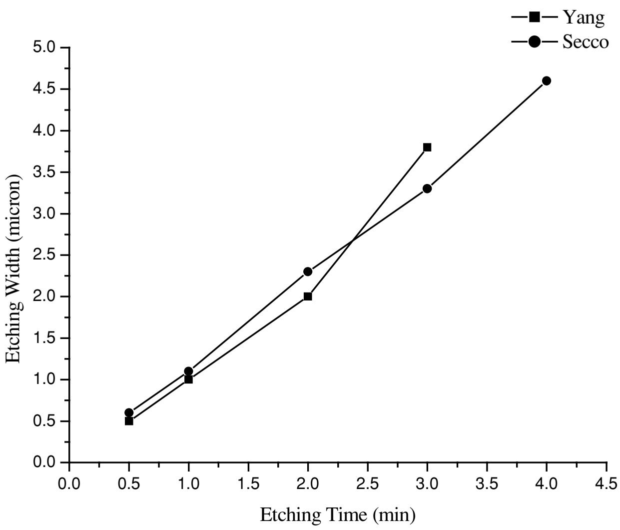

Figure 4. The etching depth versus etching time of Secco and Yang etched dislocations.

Table 2. Dislocation density values of different mc-Si producers.

mc-Si company	Dislocation density (cm^{-2})	Diffusion length (μm)
Bayer-BAYSIX	3×10^5	100
Eurosolare-EUROSIL	Weak	120–150
Solarex-SOLAREX	10^4–10^6	$\leqslant$100
Sumitomo Sitix-EMC	10^6–10^8	30–120
UDTS-Si-mc HEM	10^5–6×10^6	100

revelation on a sample previously revealed with Yang and vice versa. The aim was to enable us to make a choice between Secco and Yang for the calculation of the maximum density of defects. These tests show that the action of Secco is higher than Yang's and lead us to choose Secco for the calculation and mapping of dislocation density. This higher sensitivity of the Secco solution to defects is not due to a higher etching rate. Indeed, within the used etching time range (from 1 to 2 min), Secco and Yang solutions are comparable in dislocation etching rate (see figure 4). Moreover, in a multicrystalline silicon material, there are multiple crystallographic orientations for silicon grains, so that the sensibility to defect of a specific chemical etch is different from one grain to other. Thus, we can explain this increased sensitivity of the Secco etch to defects by probably a higher selectivity between crystalline defected areas and the remainder silicon grain zone with various crystallographic orientations.

We have compared the dislocation density and minority carrier diffusion length of our mc-Si material to other mc-Si wafers produced by major photovoltaic producers throughout the world. These parameters are given in table 2 and permit us to confirm that our material is comparable to other mc-Si materials in terms of dislocation density.

The preliminary study of the 'Secco etch' enabled us to plot the curve of the etching depth versus dipping time (see figure 4). In figure 4, we have used the maximum depth of etch pits at dislocations which are perpendicular to the surface and thus developing deeper holes. The profile of etched dislocation

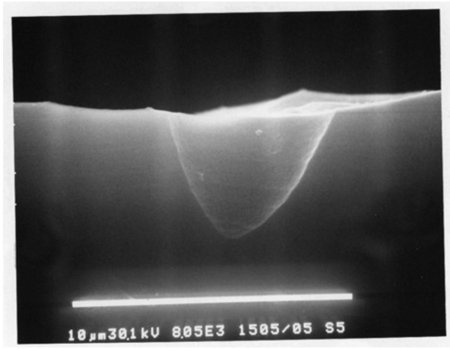

Figure 5. Cross section of dislocation delineated by Secco for 5 min.

pits delineated by the Secco solution is shown in figure 5. The dipping time of the Secco delineation process was fixed at 5 min for the following defect mapping study. Such a dipping time removes 5 μm of the dislocation zone as shown in the SEM micrograph (figure 5) and curve of figure 4.

This fine knowledge and control of crystalline defect decoration by the '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 square 10 $\times$ 10 cm^2 mc-Si wafer was completed, we submitted the wafer to a Secco etch during 5 min. We chose this revelation time (the longest tried so far) in order to strongly mark the defected zones and thus obtain an appreciable variation of the sheet resistance. The mc-Si wafer revealed in this way was precisely placed under the four-probe tester, and measurement of the sheet resistance was carried out at the initially selected positions.

We plotted the map of the sheet resistance variation ($\Delta R\square$) on the 25 selected points of the mc-Si wafer. Figure 6 shows the layout obtained for $\Delta R\square$. The next step was the superposition of the physical image of the delineated mc-Si wafer with that of the $\Delta R\square$ 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 the $\Delta R\square$ mapping. Figure 6 illustrates this original result. The analysis of these results allowed us to make the first classification for $\Delta R\square$ bands according to the delineated crystalline defect type and density. This classification is summarized in table 3. It is shown that on a clean area, without any decorated defects, a small value for $\Delta R\square$ ($\Delta R\square \leqslant 0.35\ \Omega/\square$) is measured. Values of $\Delta R\square$ from 0.7 $\Omega/\square$ to 2 $\Omega/\square$ allow us to identify an effective crystalline defect zone with variable level of dislocation density, as seen in table 3. $\Delta R\square$ values which are above 2.1 $\Omega/\square$ indicate a zone of grain boundaries or a high density of twins. Indeed, a microscopic observation by SEM has shown that zones of grain boundaries are highly and deeply Secco etched.

Finally, by using this interesting correlation between the sheet resistance variation ($\Delta R\square$) and defect density, we have plotted the mapping of the average dislocation density on a whole mc-Si wafer (see figure 7). These mapped values are in good agreement with those obtained from the SEM analysis by counting etch pits (see figure 8). After slicing this wafer into 20 pieces, we found an average difference from 5 to 15%

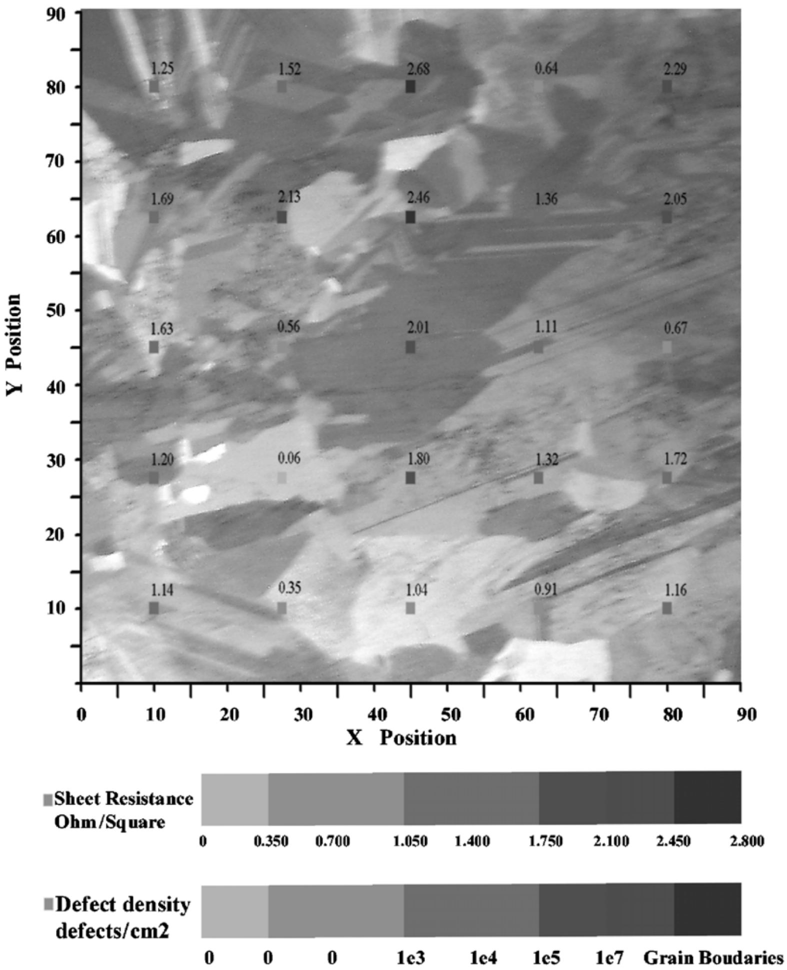

Figure 6. Superposition of the physical image of the defected area with $\Delta R\square$ mapping.

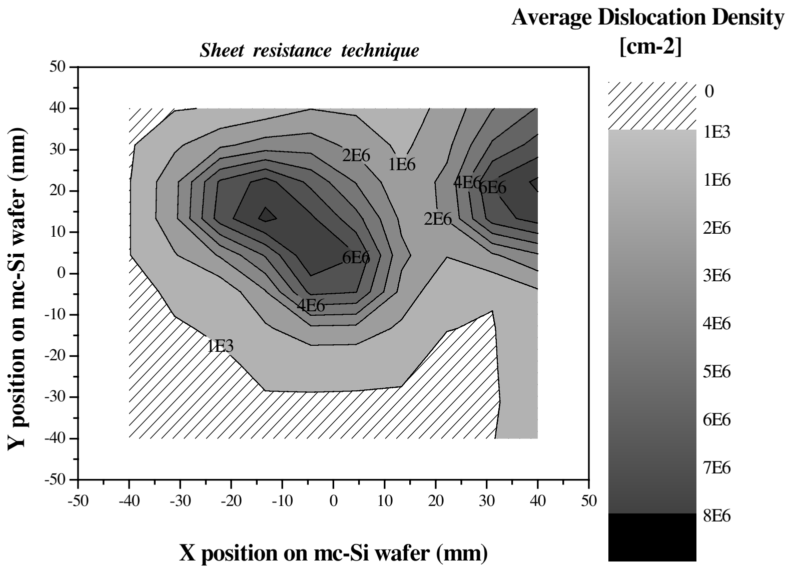

Figure 7. Mapping of the average dislocation density by using the sheet resistance technique.

for the measured dislocation density between our new method and SEM counting of etch pits.

The sheet resistance mapping with the four-probe technique has less resolution (about 3 mm) than the automated optical microscopy mapping technique. However, it gives sufficient information about defect distribution for photovoltaic device manufacturing. We believe that our developed technique is a good tool for making a quick

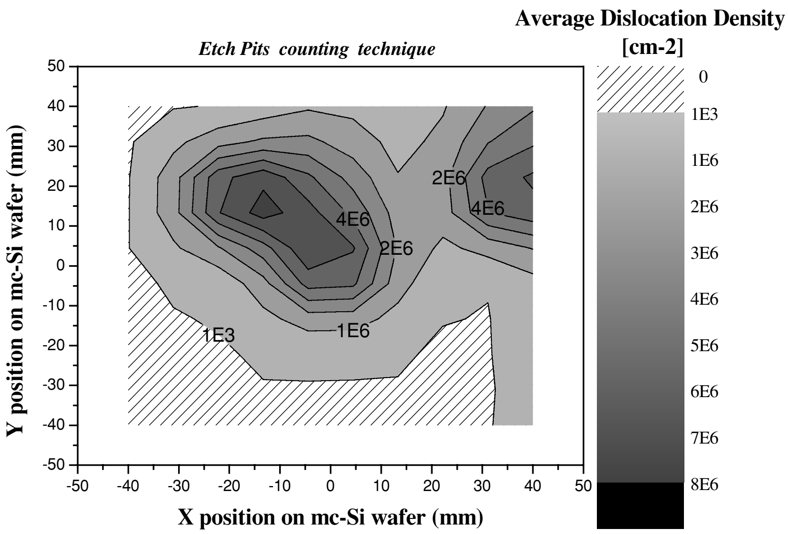

Figure 8. Mapping of the average dislocation density by using the etch pits counting technique.

Table 3. Classification of defect types according to sheet resistance variation bands.

$\Delta R\square$ bands ($\Omega/\square$)	Identification and density of defects (Nd)
$\Delta R\square \leqslant 0.35$	Clean area without any defects
$0.35 \leqslant \Delta R\square \leqslant 0.7$	Area with very low dislocation density $10\ \mathrm{cm}^{-2} < \mathrm{Nd} < 100\ \mathrm{cm}^{-2}$
$0.7 \leqslant \Delta R\square \leqslant 1.050$	Zone of low dislocation density $100\ \mathrm{cm}^{-2} < \mathrm{Nd} < 10^3\ \mathrm{cm}^{-2}$
$1.050 \leqslant \Delta R\square \leqslant 1.400$	Zone of medium dislocation density $10^3\ \mathrm{cm}^{-2} < \mathrm{Nd} < 10^4\ \mathrm{cm}^{-2}$
$1.400 \leqslant \Delta R\square \leqslant 1.750$	Zone of high dislocation density $10^4\ \mathrm{cm}^{-2} < \mathrm{Nd} < 10^5\ \mathrm{cm}^{-2}$
$1.750 \leqslant \Delta R\square \leqslant 2.100$	Zones of very high dislocation density $10^5\ \mathrm{cm}^{-2} < \mathrm{Nd} < 10^7\ \mathrm{cm}^{-2}$
$2.100 \leqslant \Delta R\square \leqslant 2.450$	Twins area and/or grain boundaries
$2.450 \leqslant \Delta R\square \leqslant 2.800$	Zones of grain boundaries

diagnostic of average defect distribution in the mc-Si wafer and grown ingot.

4. Conclusion

In this study, we have proved the feasibility of a new technique for the detection and mapping of crystalline defects on a whole mc-Si wafer area. This method is based on the exploitation of the variation of the sheet resistance ($\Delta R\square$) of Secco delineated defective zones. We have presented the first classification connecting directly $\Delta R\square$ bands to crystalline defect types and densities. These results are in good accordance with physically observed defect density and grain boundaries repartition. We have successfully optimized Secco and Yang etching parameters for the sharpest crystalline defect delineation on the mc-Si bulk material grown under the HEM process. A comparative study of these two etches has shown that the Secco etch has the best sensitivity to crystalline extended defects in the mc-Si material; therefore it is recommended for the calculation and mapping of dislocation density.

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References

[1] Karilahti M 2003 *PhD Thesis* Helsinki University of Technology
[2] Macdonald D H 2001 *PhD Thesis* The Australian National University
[3] Spiegel M 1998 *PhD Thesis* Konstanz University of Physics
[4] Yakimov E B 1997 *J. Phys. III France* **7** 2293–307
[5] Popov V G 2000 *Semicond. Phys. Quantum Electron. Optoelectron.* **3** 479–88
[6] Klukarni M S, Libbert J and Keltner S 2002 *J. Electrochem. Soc.* **149** G153–65
[7] McGuire G E (ed) 1988 *Semiconductor Materials and Process Technology Handbook* (Park Ridge, NJ: Noyes Publications) pp 46–79
[8] Dash W C 1956 *J. Appl. Phys.* **27** 1193
[9] Sirtl E and Adler A Z 1961 *Z. Metallkd* **52** 529
[10] Secco d'Aragona F 1972 *J. Electrochem. Soc.* **119** 948
[11] Yang K H 1984 *J. Electrochem. Soc.* **131** 1140
[12] Yang K H 1984 *Semiconductor Processing ASTM STP 850* ed D C Gupta (Philadelphia, PA: American Society for Testing and Materials)
[13] Jenkins W M 1979 *J. Electrochem. Soc.* **124** 479
[14] Sopori B L 1988 *J. Electrochem. Soc.* **135** 2601–7
[15] Sopori B L, Murphy R and Marshall C 1993 *23rd IEEE Photovoltaic Specialists Conference* p 190
[16] Pizzini S 1999 *Phys. Status Solidi* a **171** 123