Metal impurities profile in a 450kg multi-crystalline silicon ingot by Cold Neutron Prompt Gamma-ray Activation Analysis

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1. Introduction

Metal impurities are harmful to multi-crystalline silicon solar cells. They reduce solar cell conversion efficiencies through increased carrier recombination.[1] They are present as isolated point-like impurities or precipitates. This work is to study the concentration profiles of some metal impurities of the directionally solidified 450kg multi-crystalline silicon ingot grown for solar cell production.[2]

The concentration of such impurities are generally below $10^{15}cm^{-3}$, and as such cannot be detected by physical techniques such as secondary-ion-mass spectroscopy(SIMS).[3,4] So, we have tried to apply Cold Neutron – Prompt Gamma ray Activation Analysis(CN-PGAA) at the HANARO reactor research.

2. Methods and Results

2.1 Multi-crystalline ingot

In this experiment, a DS Furnace manufactured by Wonkwang university is employed(Fig 1). Silicon was melted in the graphite crucible by induction heating. The graphite crucible wall was coated with Si_3N_4 powder by spray coating.[5] The thickness of Si_3N_4 coating was about 25μm. The graphite resistance heating device provides heat so that there are no significant temperature variations during the melt of the silicon.

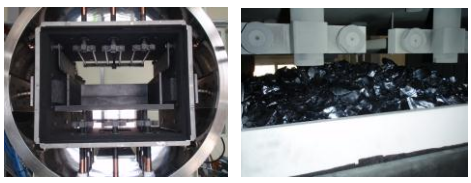

Fig 1. DS Furnace

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The feedstock was 5N grade poly-silicon. The furnace was evacuated to 2~5 Pa by a rotary pump and then 99.9% Ar gas was introduced. The growth rate average 6mm/h.

During growth, the temperature in the heat-zone is lowed in to further facilitate heat extraction from its bottom and to keep the gradients low. Fig 2. Shows a 450kg multi-crystalline silicon ingot.

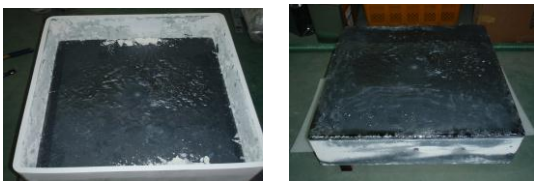

Fig 2. 450kg multi-crystalline silicon ingot

2.2 Wafer processing

The multi-crystalline ingot analyzed was a standard, boron-doped(1-2Ω · cm) ingot from a commercial process for solar cell production. The ingot are then sawn vertically into bricks and then horizontally sliced. Usually, sections of 2cm both from the top and bottom of the bricks should be cutted out before wafering, as these sections have high impurities concentration due to solid-state diffusion from the crucible at the bottom and the impurities segregation at the top. But in this case, these sections were retained in order to investigate the impurities profiles along the vertical direction.

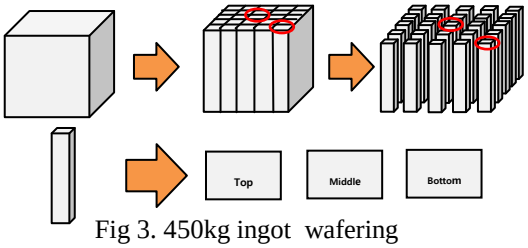

Fig 3. 450kg ingot wafering

2.3 PGAA Analysis

PGAA involves bombarding the material to be analyzed with neutrons and measuring the characteristic γ -rays produced by the elements in the sample. After the nucleus is excited by neutron capture, prompt γ -rays with specific energy are released within 10^{-14} seconds.[5]

PGAA is a rapid non-destructive radio-analytical technique capable of simultaneous, in situ, multi-element analysis, from light elements to heavy ones.

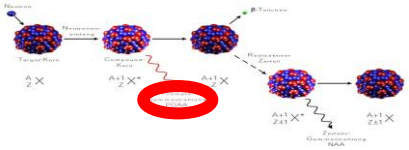

Fig 4. Diagram illustrating the process of neutron capture by target nucleus followed by the emission of gamma ray

In the overall of multi-crystalline silicon ingot, each block is not same the concentration of impurities. In principle, the block with position in the center region of ingot have the low impurities compare with the block at the edge of the ingot. With this reason, the assessment of the metal impurities in the multi-crystalline silicon are performed by using the PGAA at different positions in the ingot. In this study, two selected samples are chosen with this position at the center and the edge of the ingot(Fig 3).

Before PGAA, we cleaned the ingots with IPA, acetone, DI water and ball-milled the sample by 250rpm in 20minutes .

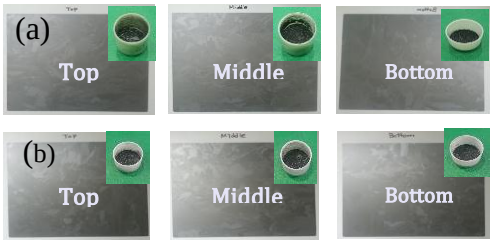

Fig 5. (a) Block A (b) Block B

A weight of the samples was 200 to 250mg. The samples were located at PGAA sample stage for 84600 seconds with a cold-neutron flux of $6*10^8$ n/cm^{2}s. The analysis was in principle, based on the Absolute method.

Fig 6. PGAA Equipment

3. Results and Discussion

The PGAA results are shown in the Table I. Table I shows a comparison of the metal impurities of the two block. Main metal impurities one Al, Ag, Mg, Cu, Mn and Mo and so on(Table 1).

Table I: Metal concentration by Prompt gamma-ray activation analysis of two types of multi-crystalline silicon material : *Block A(center of the ingot) and Block B(edge of the ingot)*

	Block A			Block B		
	Top	**Middle**	**Bottom**	**Top**	**Middle**	**Bottom**
Ag	**6.25E+03**	**6.19E+03**	**6.25E+03**	**2.57E+04**	**1.23E+04**	**1.91E+04**
Au	2.15E+02	2.05E+02	2.40E+02	3.86E+02	3.05E+02	3.74E+02
Al	**2.47E+03**	**2.35E+03**	**2.44E+03**	**1.36E+04**	**1.31E+04**	**1.37E+04**
Cl	1.33E+02	8.59E+01	8.79E+01	1.36E+04	1.31E+04	1.37E+04
Cu	**-**	**-**	**-**	**2.3E+03**	**1.01E+03**	**2.02E+03**
Mg	**1.33E+03**	**1.30E+03**	**1.66E+04**	**8.09E+04**	**7.82E+03**	**8.22E+04**
Mn	**4.21E+01**	**3.74E+01**	**4.37E+01**	**5.10E+01**	**4.68E+01**	**4.87E+01**
Mo	**1.41E+04**	**1.67E+03**	**2.00E+03**	**3.46E+04**	**3.40E+04**	**3.56E+04**
Nb	9.3E+02	9.14E+02	1.37E+03	7.15E+04	7.16E+02	7.25E+04
Pt	1.70E+03	1.36E+03	1.89E+03	1.94E+03	1.83E+03	1.90E+03

Both the block A and B concentrations of impurities the middle regions of the ingot, are low(Fig 7). Sharply impurities increased towards the top of the ingot due to the segregation into the melting phase, while the impurities sharply increased towards the bottom probably due to the solid state diffusion.

The higher impurity concentration in the block B that in the block A, can be explained by contamination from crucible and its coated wall.

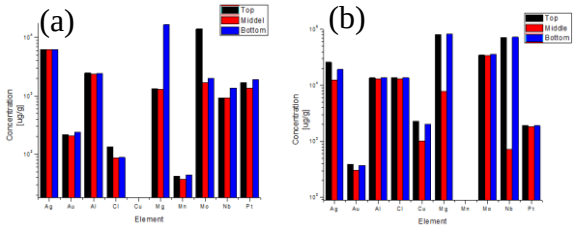

Fig 7. Metal concentration by PGAA : *Block A(center of the ingot) and Block B(edge of the ingot)*

4. Conclusions

The impurity concentrations of Au, Mn, Pt, Mo of a photovoltaic grade multi-crystalline silicon ingot appear by segregation from the liquid to the solid phase in the central region of the ingot during the crystallization. In the impurities concentration of the bottom region is higher than middle region due to the solid state diffusion. Towards the top region the segregation impurities diffused, during cooling process.

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