

## Characterization of Amorphous Silicon by Secondary Ion Mass Spectrometry

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### ABSTRACT

Based on various implanted standards, we have used SIMS (Secondary Ion Mass Spectrometry) to characterize amorphous Si thin films with high hydrogen content. SIMS and HFS (Hydrogen Forward Scattering) showed good agreement on the measured total H doses for H-implanted Si samples and the a-Si thin films. For the H-implanted Si samples, in the dose range of  $2 \times 10^{15}$  atoms/cm<sup>2</sup> to  $2 \times 10^{17}$  atoms/cm<sup>2</sup> (corresponding to peak H concentration from 0.32 at.% to 32 at.%), SIMS results showed that the calibration curve is a straight line. In other words, no correction for SIMS quantification is needed when moving from low to high hydrogen content samples. Analysis of P (Phosphorus) in a-Si thin films requires the use of high mass resolution magnetic sector SIMS to separate P and a mass interference from (<sup>30</sup>Si+H). Using a magnetic sector SIMS instrument, P-doped a-Si thin layers (~ 50nm thick) were analyzed using 3keV O<sub>2</sub> beam with oxygen leak for better depth resolution and improved detection limits. For the analysis of C, N, O in a-Si thin films (again approximately 50nm thick) the profiling energy typically needs to be lowered down to 3keV and the material needs to be sputtered at a high rate in order to reach real background levels. In this work, a-Si thin films were also analyzed using a 3keV Cs<sup>+</sup> primary ion beam with (Cs<sub>2</sub>M)<sup>+</sup> (M= C, N, O) detection for good depth resolution and detection limits.

### INTRODUCTION

Impurities and dopant profiles in amorphous silicon are important aspects for a-Si(H) solar cell materials [1] and a-Si TFT (Thin Film Transistors) for flat panel display applications [2]. To material engineers, a new challenge is to make more controllable thinner a-Si films for subsequent manufacture into devices. One way to reduce the cost of solar electricity is to reduce the thickness of the films that form a solar cell [1]. It is well known that hydrogen content is key to the optimized function of a-Si(H) solar cells and a-Si TFT devices for flat panel displays [1,2]. For example, it has been reported that by switching a-Si TFT to poly-Si TFT, the mobility can increase from  $<1$  cm<sup>2</sup>/Vsec (for a-Si) to  $>200$  cm<sup>2</sup>/Vsec (for poly Si). The higher mobility can result in smaller thin film transistors, higher image resolution, lower power consumption and better performance. The production of low hydrogen content a-Si is essential for laser-induced crystallization of a-Si for poly-Si TFT applications. Because of these new manufacturing demands there are also new characterization challenges for SIMS and other material characterization techniques.

In this paper we report some examples of SIMS analyses of a-Si thin films (down to approximately 50nm thick), using both Cs<sup>+</sup> and O<sub>2</sub><sup>+</sup> primary ion beams generated by Cameca magnetic sector SIMS and PHI quadrupole SIMS instruments. The various analytical modes used and typical results obtained are highlighted in the six areas (see the context).

### EXPERIMENTAL DETAILS

Dynamic SIMS instruments use two kinds of mass analyzers, magnetic sectors and quadrupole mass filters [3,4,5]. Cameca magnetic sector SIMS tools and PHI quadrupole SIMS tools at Charles Evans & Associates in Sunnyvale, CA, were used to analyze the implanted standards and a-Si thin films for this work. Table I lists the instrument conditions used for analyzing specific elements within a-Si thin films. These selections are based on a combination of general knowledge on SIMS analysis [3,4,5], prior practical experience and actual data from test samples. It should be noted that the selection of the

**TABLE I.** Instrumental conditions used for this work.

Condition #	1	2	3	4
<i>Instrument</i>	Cameca Magnetic sector	Cameca Magnetic sector	PHI Quadrupole	PHI Quadrupole
<i>Elements Monitored</i>	H, C, N,O, F, S, Cl	P, Al, Cr, Fe, Cu	H, C, N, O, F, S, Cl	Li, Na, K
<i>Primary Ion Beam</i>	Cs <sup>+</sup>	O <sub>2</sub> <sup>+</sup>	Cs <sup>+</sup>	O <sub>2</sub> <sup>+</sup>
<i>Primary Ion Energy</i>	2.5keV to 14.5keV	2.5keV to 5.5keV	2.5keV to 5keV	2.5keV to 5keV
<i>Positive or Negative Secondary Ions Monitored</i>	(Cs <sub>2</sub> M) <sup>+</sup> : M=H,C,N,O etc, or H <sup>-</sup> , C <sup>-</sup> , (Si+N) <sup>-</sup> , O <sup>-</sup> , F <sup>-</sup> , P <sup>-</sup> , S <sup>-</sup> ,Cl <sup>-</sup>	P <sup>+</sup> , Al <sup>+</sup> , Cr <sup>+</sup> , Fe <sup>+</sup> , Cu <sup>+</sup>	H <sup>-</sup> , C <sup>-</sup> , (Si+N) <sup>-</sup> , O <sup>-</sup> , F <sup>-</sup> , S <sup>-</sup> ,Cl <sup>-</sup>	Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>
<i>Oxygen Leak to main chamber</i>	No	Yes for P, No for others	No	No

profiling energy is dependent on the thickness of the a-Si thin films and the energies used ranged from 2.5 to 14.5keV. In general, the quadrupole SIMS tools are easier to tune and operate at low profiling energy for both positive and negative secondary ion detection since the sample voltage is at ground. In contrast, magnetic sector SIMS tools are easier to operate at low profiling energy with only positive secondary ion detection. In addition, if the samples have a layer structure containing insulating layers, then during SIMS analyses a charge neutralizing electron gun can be used for charge compensation.

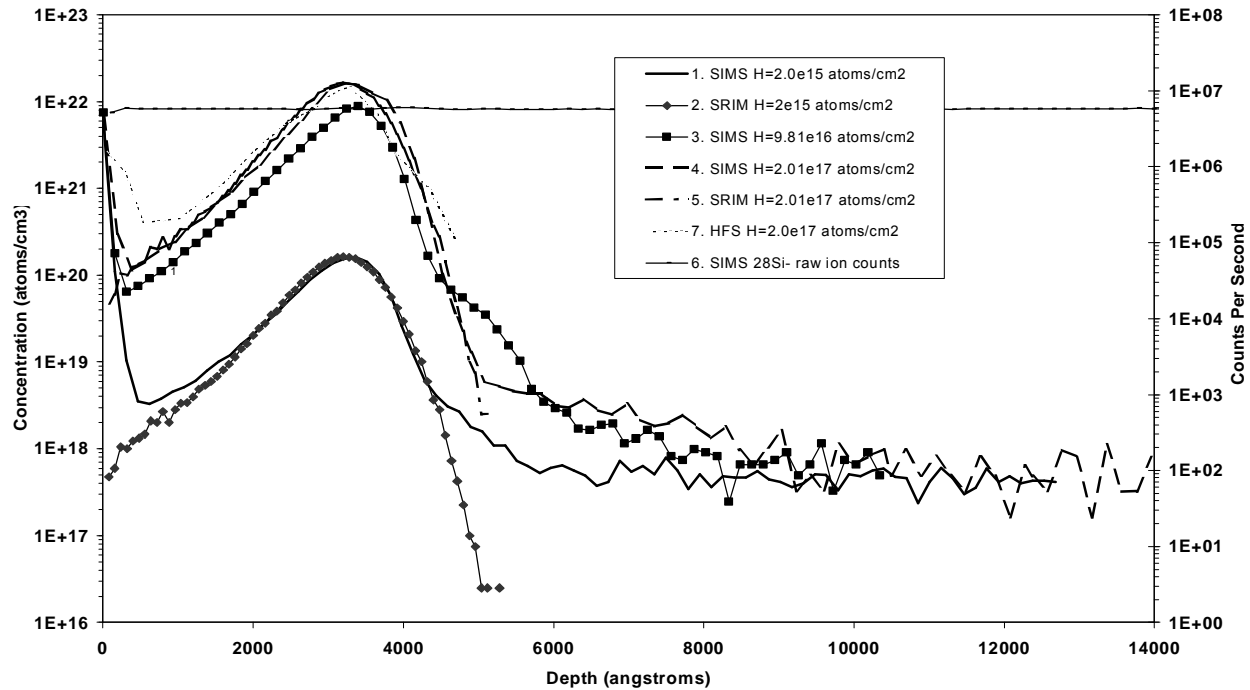
It should be noted that the analysis of phosphorus (P) in a-Si thin films containing a high H content requires the use of a magnetic sector SIMS tool, which can be tuned and operated at high mass resolution setting to completely separate P from (<sup>30</sup>Si+H). Here the mass resolution is defined as  $M/\Delta M$ , where M is the mass monitored and  $\Delta M$  is the mass separation of the interfering peak [5]. For example, P has a mass at 31.9738 mass units and (<sup>30</sup>Si+H) has a mass at 31.9816 mass units. The mass difference between P and (<sup>30</sup>Si+H),  $\Delta M$ , is equal to 0.0078 mass units, therefore, a mass resolution of  $M/\Delta M > 3956$  is needed to measure P in a-Si thin films containing high levels of H. A magnetic sector SIMS tool can be tuned to work at  $M/\Delta M = 10000$ , whereas a quadrupole SIMS tool normally operate at only  $M/\Delta M = 200$ .

Hydrogen contents in some implanted Si samples and a-Si films were also analyzed with HFS (Hydrogen Forward Scattering) for comparison. HFS spectra were obtained with 2.3MeV <sup>4</sup>He<sup>++</sup> beam and a scattering angle of 30 degree, using a National Electrostatics Corporation accelerator.

## RESULTS AND DISCUSSION

### Analysis of Hydrogen in a-Si films:

Hydrogen profiles in silicon are normally obtained with Cs<sup>+</sup> primary beam bombardment and measure negative H<sup>-</sup> secondary ions or positive (Cs<sub>2</sub>H)<sup>+</sup> secondary ions. It should be noted that normally the SIMS quantification is based on implanted standards. It has been observed by various authors that the calibration curves are straight lines in the low concentration range (generally below 1 at.%) [3,4,5]. When the impurity level is above 1 at.% of matrix, the secondary ion yield may vary non-linearly with increasing impurity level. Since we focused on a-Si films containing a high level of H (say up to 30 at.%), it was necessary to study if the H secondary ion yield increased linearly with increasing H in a-Si. To do this, it was necessary to use HFS since it provided an independent analytical method to determine the H content in Si at high levels (i.e. total areal density of H in unit of atoms/cm<sup>2</sup>, or atomic percentage if the H was distributed uniformly in the a-Si film). However, HFS typically has much worse depth



**Figure 1.** A number of simulations (by SRIM code [6]) of H implants into Si and also SIMS and HFS data from those actual implants.

resolution than SIMS and also a poorer detection limit (approximately 0.2 at.% at best) compared with (approximately 0.0001 at.% at best). HFS is most suited to a-Si samples that have a uniformly distributed high H content.

Line 1 on Figure 1 shows the hydrogen SIMS depth profile for Si implanted with 30keV  $^1\text{H}^+$  with a dose of  $2\text{e}15$  atoms/cm $^2$ . Line 2 shows the simulated H depth profile by SRIM (The Stopping and Range of Ions in Matters) computer code [6] for the same implantation. The SIMS profile was obtained by 14.5keV  $\text{Cs}^+$  primary beam and monitored  $\text{H}^-$  and  $^{28}\text{Si}^-$  (see Table 1, instrument condition 1). It can be seen that the agreement between the measured and simulated H depth profiles are very good. The implantation resulted in a skewed-Gaussian-like H distribution in Si, and the peak concentration is  $1.61\text{e}20$  atoms/cm $^3$  (i.e. about 0.32 at.%). Line 3 shows the H depth profile on another Si sample implanted with 30keV  $^1\text{H}^+$  with a dose of  $1.0\text{e}17$  atoms/cm $^2$ . This depth profile was obtained using the same conditions as those from line 1, discussed above. The measured H dose is  $0.981\text{e}17$  atoms/cm $^2$  (with error bars approximately  $\pm 10\%$ ). In other words, we obtained the RSF (relative Sensitivity Factor) value [3,4,5] from the sample implanted with  $2\text{e}15$  H atoms/cm $^2$  and applied same RSF value to the other samples.

Line 4 (SIMS) and line 5 (SRIM) on Figure 1 show measured and simulated H depth profiles for a Si sample implanted with 30keV  $^1\text{H}^+$  to a high dose of  $2.0\text{e}17$  atoms/cm $^2$ . Line 6 is the simultaneously measured raw  $^{28}\text{Si}^-$  ion counts acquired with the  $\text{H}^-$  signal. The  $^{28}\text{Si}^-$  profile shows a very little ion yield variation around the H peak. It should be noted that,  $^{28}\text{Si}$  rather than  $^{30}\text{Si}$  was monitored as the matrix signal since  $^{30}\text{Si}$  has an interference from ( $^{29}\text{Si}+\text{H}$ ). The quantification of line 4 was based on the RSF value obtained from line 1 (i.e. from the  $2\text{e}15$  atoms/cm $^2$  implanted standard). For the high dose H-implanted Si sample, the measured dose was  $2.01\text{e}17$  atoms/cm $^2$ . It is the same as the nominal dose of  $2.0\text{e}17$  atoms/cm $^2$ . The measured H peak concentration is about  $1.60\text{e}22$  atoms/cm $^3$  (i.e. approximately 32 at.% in Si) and the measured H depth profile is still a Gaussian-like distribution. Like the low dose

**Table II.** Comparison of the total H dose on typical samples measured by SIMS and HFS.

<i>Sample ID (dose in atoms/cm<sup>2</sup>)</i>	Total H dose by SIMS (atoms/cm <sup>2</sup> )	Total H dose by HFS (atoms/cm <sup>2</sup> )
#1: <i>H implanted Si</i> <i>Nominal dose: 2.0e15, 30keV</i>	(2.0±0.2)e15 (line 1 in Figure 1)	Below the detection limit of the HFS
#2: <i>H implanted Si</i> <i>Nominal dose: 5.0e16, 170keV</i>	(4.97±0.5)e16	The average H is near the HFS detection limit (0.2at.%).
#3: <i>H implanted Si</i> <i>Nominal dose: 1.0e17, 30keV</i>	(9.81±0.98)e16 (line 3 in Figure 1)	(1.05±0.11)e17
#4: <i>H implanted Si</i> <i>Nominal dose: 2.0e17, 30keV</i>	(2.01±0.2)e17 (line 4 in Figure 1)	(2.0±0.2)e17 (line 7 in Figure 1)
#5: <i>195nm a-Si film</i>	(9.86±1)e16	(8.63±0.9)e16
#6: <i>300 nm a-Si film</i>	(3.96±0.4)e17	(3.62±0.36)e17

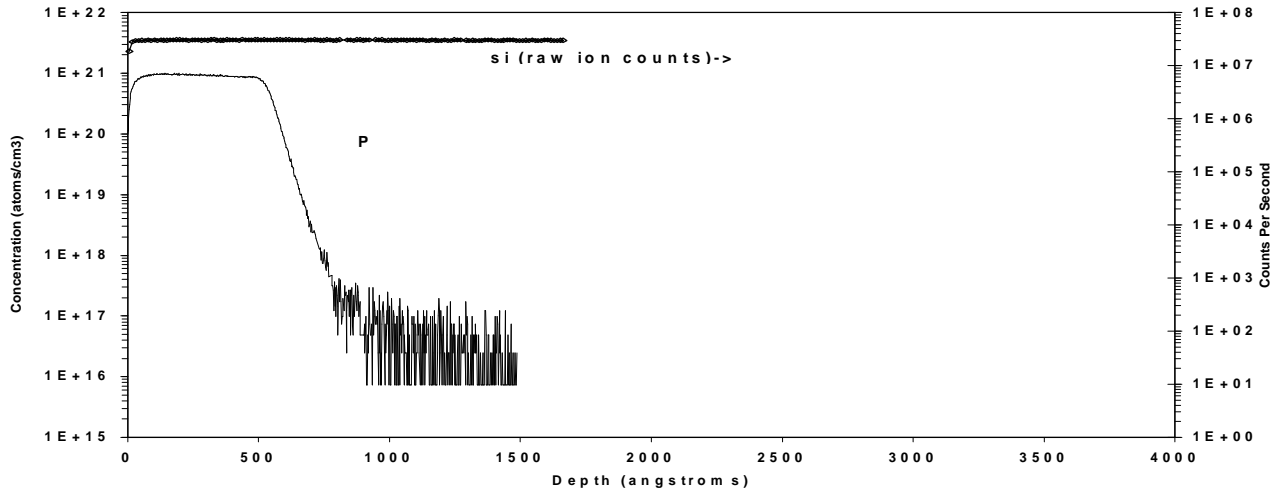
case, the measured H depth profile by SIMS is in good agreement with the simulated profile by SRIM (based on a Monte Carlo simulation). Line 7 on Figure 1 shows the H depth profile for same implanted sample (i.e. 2e17 atoms/cm<sup>2</sup>) measured by HFS, the measured total dose is 2.0e17 atoms/cm<sup>2</sup> (with the error bars of ±10%). It can be seen that the depth resolution and the detection limit of HFS on the Gaussian-like distribution is clearly poorer than the SIMS data.

From the above results and discussion, it can be seen that the implanted H peak increased linearly with increasing the dose and no correction on the RSF value was needed when moving from low hydrogen content Si sample to high hydrogen content Si sample. Table II shows a comparison of the measured total hydrogen doses by SIMS and HFS. It is clear the agreement between the SIMS results and HFS results are good. In summary, the above results clearly showed that the yield of H secondary ions increase linearly with increasing H content and the SIMS calibration curve [3] for H in Si is a straight line.

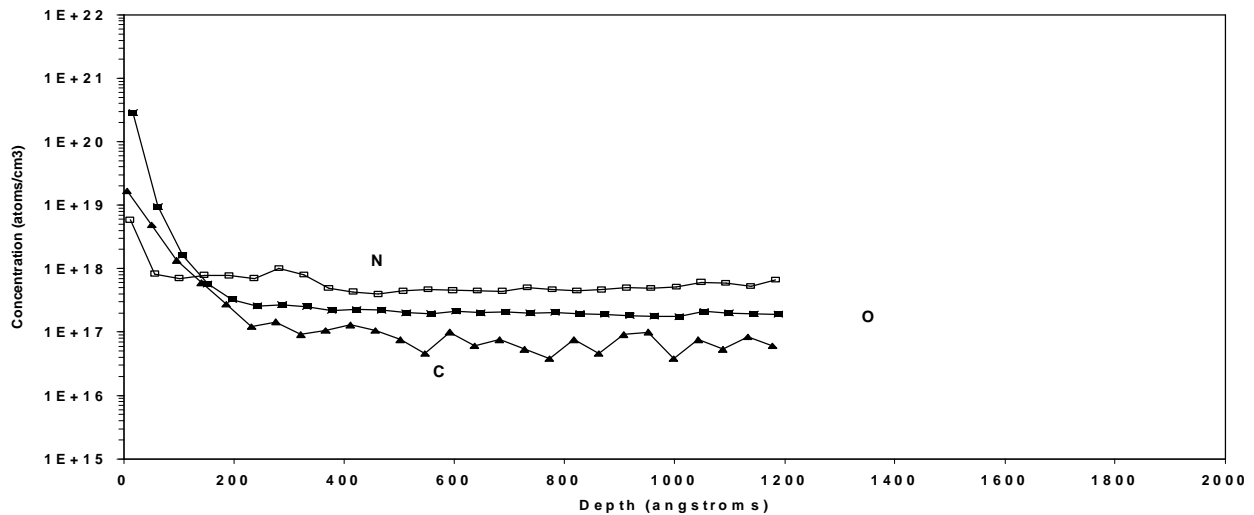
### **3.2. Analysis of Phosphorus doped n+-type a-Si films**

Phosphorus is normally used as n-type dopant for a-Si and SIMS can measure the dopant concentration vs the depth scale. As we have discussed above, it is necessary to use a magnetic sector SIMS tool to measure P in a-Si films since only this type of SIMS tool has sufficient high mass resolving power. In addition, the P-doped layer could be as thin as 50nm, followed by an undoped a-Si layer. With both layers having high levels of H, it is clear that good depth resolution and good detection limit are required in this case. Reducing the primary ion beam energy can improve the depth resolution since primary beam mixing effects are reduced at lower energies [3]. In this work, 3keV O<sub>2</sub> ion beam with oxygen O-leak technique with 4000 mass resolution was used to analyze a thin P-doped layer. In this case, the oxygen leak technique can improve the detection limit for P and reduce the sputter-induced roughness [3,5].

Figure 2 shows a P depth profile through a 50nm P-doped a-Si layer followed by an undoped a-Si layer, with the raw Si ion counts. The interface between the P-doped layer and non-doped layer is quite sharp. The depth resolution was 6.8nm/decade. Here the depth resolution is defined as the interface width per decade signal drops in the exponential of the measured P profile [3]. It should be noted that this number included the contribution of the initial surface roughness of this a-Si film (about 2.9nm, measured by profilometer), the actual waviness of the interface, and the primary beam induced mixing effects [3,4,5]. The approach used for P determination in a-Si films is likely to be the best available for SIMS depth profiling of such P-doped layers with high H content.



**Figure 2.** SIMS depth profile of Phosphorus in the partially P-doped a-Si layer.



**Figure 3.** SIMS depth profiles of C,N and O in a-Si obtained using 3keV  $\text{Cs}^+$  and monitoring  $(\text{Cs}_2\text{M})^+$ .

#### **Analysis of C,N,O in a-Si thin films:**

High levels of C, N, and O can affect the mobility of electrons in a-Si films and so they have to be monitored and kept within controlled levels. SIMS depth profiling of trace levels of atmospheric species in a-Si needs good vacuum within the analytical chamber. A higher sputtering rate typically produces better detection limits [4]. In addition, the thin layer required a lower primary beam energy. The mixing effects of a 12keV  $\text{Cs}^+$  primary beam would likely induce about 15nm decay length per decade and lowering the primary beam energy to 3keV would significantly reduce the decay length. However, reducing the primary energy can make it more difficult to get fast sputter rates, therefore there are some challenging issues here. We have found that using a Cameca magnetic sector SIMS tool, 3keV  $\text{Cs}^+$  beam and monitoring positive molecular species  $(\text{Cs}_2\text{M})^+$  ( $\text{M}=\text{C},\text{N},\text{O}$ ) can well meet the above requirements.

Figure 3 shows the C, O and N depth profiles from an a-Si sample, obtained with a 3keV  $\text{Cs}^+$  primary beam and the detection mode discussed above. The detection limits for C, N, O are  $2\text{e}16$ ,  $1\text{e}17$ , and  $1\text{e}16$  atoms/cm<sup>3</sup>, under normal profiling condition for thin layers. All measured impurities of C, N and O shown in Figure 3 are real and are above the detection limits.

### **Analysis of F and S in a-Si thin films**

We have found that if the measured oxygen level and hydrogen level are high in an a-Si film, then if S and F are required then they should be analyzed by magnetic sector SIMS in order to eliminate of mass interferences of ( $^{16}\text{O}+^{16}\text{O}$ ) for  $^{32}\text{S}$  or ( $^{18}\text{O}+\text{H}$ ) for  $^{19}\text{F}$ . In this case, a mass resolution of  $M/\Delta M=2220$  is needed for analysis of S and F. If the O level and H level are low, F and S can also be analyzed by quadrupole SIMS tool.

### **Analysis of Li, Na, F, K, Cl in a-Si thin films**

As possible contaminants, these species can be sources of mobile ionic charge at the a-Si/SiO<sub>2</sub> interface. Therefore, it is very important to monitor and control the oxide charge in the gate oxide layer overlaid on a-Si films.

It has been reported that Na in the oxide layer can move during the SIMS analysis if an electron gun was used for charge compensation [4]. Quadrupole SIMS data can be acquired with a very low electron gun energy and thus reduce such possible Na diffusion during SIMS profiling. Therefore, we have used 3-5keV O<sub>2</sub> on a quadrupole SIMS tool to profile Li, Na, and K, and we have also used 3keV Cs<sup>+</sup> on a quadrupole SIMS tool to profile Cl.

### **Analysis of Al, Cr, Fe, Ni, and Cu**

These species are possible metallic contaminants during a-Si thin film preparation. In practical applications, the a-Si layer is normally followed by an oxide or nitride layer. The metallic contaminants are either fast or slow diffusers in the oxide layer, and will likely lower the breakdown voltage of the oxide layer, therefore, they have to be monitored and controlled.

SIMS analysis of these metallic contaminants needs to use magnetic sector SIMS tools and operating at medium mass resolution ( $1000 < M/\Delta M < 3000$ ) or high mass resolution ( $M/\Delta M > 3000$ ). For example, for Ni,  $M/\Delta M=4000$  is needed to separate  $^{58}\text{Ni}$  from ( $^{28}\text{Si}+^{30}\text{Si}$ ).

## **CONCLUSIONS**

SIMS and HFS have been used to characterize a-Si thin films. The results have shown that the yield of H secondary ions increases linearly with increasing H content and the SIMS calibration curve [3] for H in Si is a straight line over a large H concentration range. Using magnetic sector SIMS, a P-doped a-Si thin layer (50nm thick) was analyzed by using 3keV O<sub>2</sub> beam with oxygen leak. Good depth resolution and detection limit have been obtained. 3keV Cs<sup>+</sup> with (Cs<sub>2</sub>M)<sup>+</sup> detection was used to analyze C, N and O in a-Si thin films.

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