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## XAFS Studies of Self-Aligned Platinum Silicide Thin Films at the Pt $M_{3,2}$ Edge and the Si K-Edge

S.J. Naftel, A. Bzowski, T.K. Sham, D.-X. Xu\* and S.R. Das\*

*Department of Chemistry, University of Western Ontario, London, N6A 5B7, Canada*

*\* National Research Council of Canada, Institute for Microstructural Science, Ottawa, K1A 0R6, Canada*

**Abstract.** Pt-Si thin films with the thickness of several hundred Å prepared on n-type Si(100) by UHV sputter-deposition procedures and subsequent annealing have been studied with X-ray absorption fine structure spectroscopy at the Pt  $M_{3,2}$  edge and the Si K-edge. It is found that, under favourable conditions, single phase PtSi films can be obtained. These films exhibit the same XAFS characteristics as those of bulk samples. The  $M_{3,2}$  edge exhibits XANES features very similar to those of the Pt  $L_{3,2}$  edge obtained from the samples. The analysis of the Pt  $M_{3,2}$  edge whiteness and the Si K-edge results show significant charge redistribution at both Pt and Si sites upon silicidation.

### 1. INTRODUCTION

Transition metal silicides are used in the microelectronics industry as Schottky barrier clamps between the base and collector for fast switching operations and for low resistance contacts to source drain and gate [1]. As the size of devices shrinks it is of paramount importance to understand the behaviour of thin films of transition metal silicides with micrometer dimensions. In this study we look at the electronic behaviour of PtSi films using XANES.

### 2. EXPERIMENTAL

The PtSi samples were created by magnetron sputter depositing layers of Pt on Si(100) crystals followed by RTA (rapid thermal annealing) procedures performed ex situ under  $N_2$  atmosphere to form the silicides as described elsewhere [2].

Both Pt  $M_{3,2}$  edges and Si K-edge spectra were taken under similar experimental conditions on the Double Crystal Monochromator beamline in the Canadian Synchrotron Radiation Facility at SRC, University of Wisconsin-Madison. InSb(111) crystals were used as the monochromator. The spectra were collected in TEY mode (specimen current) at room temperature.

Pt  $L_{3,2}$  edge XANES were recorded on the X-11A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab using a He amplified TEY detector.

### 3. RESULTS AND DISCUSSION

Figures 1 and 2 show, respectively, the Pt  $M_3$  and  $M_2$  edges of Pt metal and some representative PtSi films normalized to the edge jump. It is clear that after annealing (silicidation) the area of both whiteness increases relative to the Pt sample. The increase in area is related to the  $d$  hole counts and indicates that Pt loses  $d$ -charge in the formation of PtSi. It is interesting to note that the area of the  $M_2$  whiteness increases more rapidly than the area of the  $M_3$  whiteness, this would suggest that the loss of charge is preferentially from the  $d_{3/2}$  level.

We have recently compared the  $L_{3,2}$  and  $M_{3,2}$  edge XANES of the  $5d$  elements and shown that both can be used as a measure of the occupancy of the  $d$  states in the  $5d$  transition metals [3,4]. If we compare the PtSi films spectra to a bulk PtSi spectra from literature [5] we see that the spectra compare favourably indicating that the bulk of the films are PtSi regardless of the annealing time. The unannealed sample is almost identical to the Pt metal spectrum indicating that little silicidation takes place without annealing.

To calculate the areas under the whiteness we use the Au  $M_2$  XANES spectra, taken under similar conditions, normalized and calibrated in the same way as the other spectra and subtract it as a background [3]. The area under the difference curve is the area of the whiteness. This is reasonable as Au has no  $d$  holes and thus the  $M_2$  spectrum exhibits no whiteness and is almost an arctan edge. It is estimated that the use of the Au  $M_2$  edge and inaccuracies in the alignment of the spectra lead to an error of 5 to 10 % in the calculated areas [4]. The areas can easily be related to the  $5d$  hole count at the Pt site through the equations [6]:

$$A_2 = C_0 N_0 E_2 (R_d^{-3p/2})^2 (1/3 h_{3/2}) \quad (1)$$

$$A_3 = C_0 N_0 E_3 (R_d^{-3p/2})^2 ((6h_{3/2} + h_{5/2})/15) \quad (2)$$

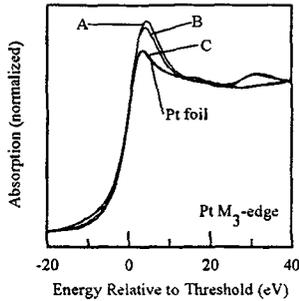


Fig. 1: Pt M<sub>3</sub>-edge XANES of Pt foil and Pt films: A) annealed 400°C, 475°C, 555°C/30 sec. (x116), B) annealed 400°C/30 sec. (x115), C) unannealed (x150f).

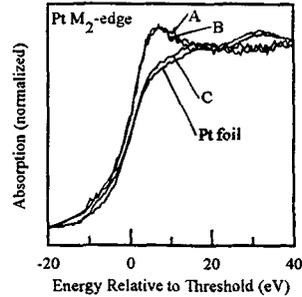


Fig. 2: Pt M<sub>2</sub>-edge XANES of Pt foil and Pt films; A) annealed 400°C, 475°C, 555°C/30 sec. (x116), B) annealed 400°C/30 sec. (x115), C) unannealed (x150f).

Using eqs. (1) and (2) we can calculate the  $h_{3/2}$  and  $h_{5/2}$  hole counts of the silicides in reference to the theoretical  $h_{3/2}$  and  $h_{5/2}$  hole counts of Pt metal [6]. The results are presented in table 1. The net result is that the ratio of holes  $h_{5/2}/h_{3/2}$  decreases towards its statistical value (1.5) as Pt loses  $d$ -charge during the formation of PtSi. Areas calculated from the Pt L<sub>3,2</sub> edges follow the same trend.

Figure 3 shows the Si K-edge XANES of Si(100) and some PtSi thin films. The large peak at ~1847 eV is attributed to a surface oxide which complicates the analysis of the Si K-edge spectra. However, since SiO<sub>2</sub> has a flat pre-edge and the spike is >7 eV above the Si threshold, it has little effect on the XANES structure for regions < 7 eV above the threshold. Furthermore the oxide peak can be removed by subtracting the SiO<sub>2</sub> contribution from the PtSi spectrum. In any case it is clear from figure 3 that Si, in the PtSi films, has a more intense whiteline and thus loses  $p$ -charge. This is in contrast to the 3d metal silicides study recently done by Weijs *et al.* [7]. The implication of Si losing  $p$ -charge is that it gains  $s$ -charge to maintain electroneutrality locally.

Table 1: Whiteline areas and  $d$  hole counts derived from the Pt M<sub>3,2</sub> edges. (the uncertainty in the areas and hole counts is not greater than 5% and 7%)

Sample	A <sub>2</sub> (eV unity abs.)	A <sub>3</sub> (eV unity abs.)	$h_{3/2}$	$h_{5/2}$	$h_{5/2}/h_{3/2}$
Pt foil	2.54	7.16	0.344	1.0	2.90
x150f	2.56	7.10	0.346	0.992	2.87
x115	5.27	7.89	0.712	1.05	1.47
x116	5.32	8.03	0.719	1.07	1.48

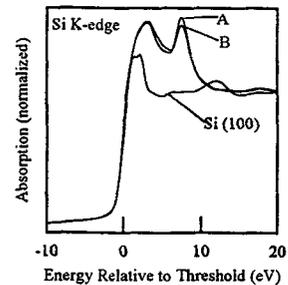


Fig. 3: Si K-edge XANES of Si(100) and PtSi films; A) x116 and B) x115.

4. SUMMARY

We have reported the Pt M<sub>3,2</sub> and Si K-edge XANES for a series of PtSi films. The as-deposited Pt layers do not form silicides. When annealed a layer of PtSi is formed. Analysis of the whiteline areas showed significant charge redistribution on silicidation with the Si site losing  $p$ -charge and the Pt site losing  $d$ -charge such that the  $d$  hole count ratio moves towards its statistically expected value.

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