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Trace Analysis of Al on Silicon Surfaces by Ultra-soft X-Ray Emission Spectroscopy

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ABSTRACT

It is shown that near normal incidence, low-energy electron excitation of Al on silicon surfaces by ultra-soft X-Ray emission spectroscopy yielded limits of detectability (LD) in the picogram region. This result on L band emission via electron excitation is fully competitive with photon excitation using K- α lines via grazing incidence total reflection techniques (TXRF). Surprisingly, it was also found that normal incidence synchrotron photon excitation on the same sample yielded much higher values of LD than low-energy electron excitation, undoubtedly due to the use of a poor transmission grating used in the entrance optics.

Key Words: X-Ray emission spectroscopy; Al L emission; Trace analysis; Si surfaces; Electron excitation.

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INTRODUCTION

There has been an ever-increasing interest in trace analysis of all elements in general, and of light elements on Si surfaces in particular, by using X-ray fluorescence spectroscopy. Of the various methods used TXRF (total reflection X-ray fluorescence) has emerged as the most promising technique. With ordinary laboratory instrumentation and without special efforts on sample handling, TXRF has provided for heavier elements, even in the earlier days, limits of delectability (LD) values at the picogram levels.^[1] For the lighter elements, such as Na and Al, LD values could be estimated at the nanogram levels.^[1] Using either rotating anodes of high wattage or synchrotron sources, and a variety of sample handling improvements^[2-6] these LD values were lowered significantly. With the advent of improved instrumentation for detecting light elements, recent efforts have extended the analysis to light elements, such as Na and Al with LD values at the picogram levels^[7,8] via K- α lines.

We wish to report here on an experiment performed about 14 years ago,^[9,10] according to which it is possible to obtain sensitivity values with direct electron excitation of Al-L bands that compare well with those obtained with modern TRXF-K lines. We also had the opportunity in this experiment to compare these sensitivity values with those obtained by synchrotron excitation. Surprisingly, inexpensive electron excitation was found to be superior to expensive synchrotron excitation.

INSTRUMENTATION

For the synchrotron radiation, the U-ring of the NSLS facility at Brookhaven was utilized, as developed by Calcott et al.^[11] Briefly, it consists of a transmission grating in the entrance optics with a bandpass as low as 2 eV. The irradiated area is about 10 by 0.5 mm and the resultant X-ray fluorescence fills the entire slit height of the 5 M grating high speed spectrometer. Electron excitation was provided by an electron gun obtained from an old TV set which was operable from 1.0 to several kV with the bombarded sample area being roughly circular with a diameter of about 0.3 mm. In this experiment a cooled CCDA detectors was utilized.

EXPERIMENTS

For the evaluation studies, two thin films of Al were deposited by evaporation on a Si substrate with the thickness being 80 Å (Sample I) and



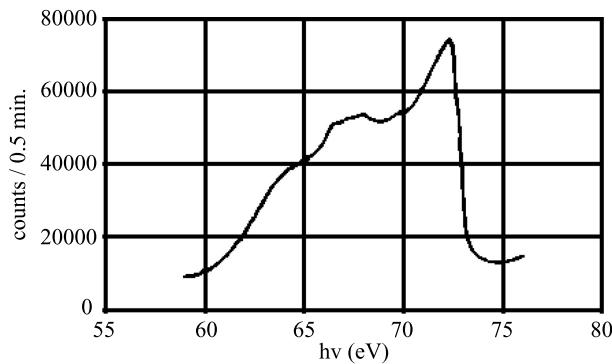


Figure 1. Sample I-80 Å Al on Si Substrate.

5 Å (Sample II). The estimated errors in thickness were approximately 5 and 10 % respectively. In order to avoid destroying Sample II, it was necessary to reduce the beam current. With the detector four-30 s. exposures were required on sample I to piece the Al L emission spectrum together, as shown in Figure 1.

The spectrum in Figure 1, for sample I, resembles that of Al metal. For sample II four-4 minute exposures were required to get the spectrum of Figure 2. With sample II the spectrum looks like that of Aluminum oxide, i.e., the entire 5 Å thick Al sample has deteriorated due to long exposure to air. The electron gun excitation conditions were about the same for both samples, namely, 132 μ A for I and 129 μ A for sample II. With sample II,

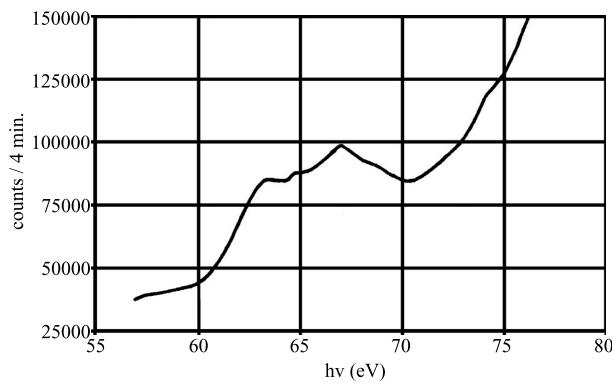


Figure 2. Sample II-5 Å on Si Substrate.



storage ring mono- chromatic photon excitation of 120 eV with a 2 eV bandpass, four-45 minute exposure times were required to obtain a reasonable spectrum.

RESULTS

If we define limit of detectability (LD) as $3\sigma_B \cdot k$, where σ_B is the standard deviation in the background (B) signal in counts, and where k equals the slope, i.e. the weight of the sample irradiated and viewed by the spectrometer divided by net line intensity (L) in counts, then one can readily calculate the LD values for a fixed time of counting. Taking the peak arbitrarily as the maximum observable peak intensity, which is at 72 eV for Al, but at 67 eV for the oxide of Al, the electron excitation value in counts/min are $L(I) = 128,000$ and $B(I) = 28,000$, $L(II) = 6,000$ and $B(II) = 12,400$. Note that with electron excitation on sample II we observe a very strong background signal from the neighboring satellites of the Si substrate. If the corresponding photon excitation values for the net line intensity and background signals are L^* and B^* , then the measured $L^*(I) = 68$ and $B^*(I) = 222$. Assuming identical slopes for photon and electron excitation, the improvement in L/\sqrt{B} in going from storage ring photon excitation to an electron gun excitation is an astonishing factor of 166. Even if one were to increase the bandpass from 2 to 200 eV, electron excitation would be significantly superior to storage ring excitation, as it was obtained that day.

The actual LD value of one minute of analysis of Al L-band with electron excitation based upon the data from sample I turns out to be 20 picograms. This value compares well with TXRF method for Al K which is reported to be in the picogram range.^[7,8] Since the electron excitation was not optimized, and the background on a Si substrate is exceptionally high, then conceivably with 20 minute exposure time Al-L on a Si substrate could be in the range of 3 to 5 picograms or lower.

CONCLUSIONS AND DISCUSSION

When we consider that the optical resolution of the spectrometer was set at 0.2 eV, coupled with the fact that the inexpensive low energy electron guns can be used in the laboratory, independent of any synchrotron, a very promising new area may be open for investigations. Since low energy excitation probably should not exceed about 1.5 kV in these studies, in order to keep the background low, we estimate that only emission lines



above about 60 Å will be suitable. Clearly more studies are needed to see just what the limits will be. As to why the synchrotron results were so poor, undoubtedly the transmission grating was not performing up to par. Subsequent checks on performance did not yield any new information, however.

As to the issue of TXRF K-radiation vs. low energy electron L-band excitation, it is too early to say just which techniques is better. To be sure with TRXF a great deal of the scattered radiation is eliminated and the signal is coming from the desired uppermost layers, but with low energy electron excitation the desired signal is coming from a very shallow depth already. Furthermore, decreasing the exit angle will also help matters by decreasing the contribution from the substrate, as shown by Andermann's^[12] group for high resolution fluorescence studies and by Nordgren's^[13] group for direct electron excitation. The additional advantage with our results is that we get chemical bonding information since we are studying valence electron transitions, whereas TXRF, as it is currently practiced, is strictly for elemental analysis.

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