Atomic Sputtering in the Analytical Electron Microscope

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Abstract

The advent of UHV medium voltage electron microscopes has brought the microanalyst to a regime of operating conditions in which electron beam induced damage can now be introduced to metallic specimens of medium to high atomic number. We report upon calculations of electron beam induced atomic sputtering which will have bearing upon the next generation of medium voltage analytical electron microscopes. The cross-section calculations reported herein have been completed for all solid elements of the periodic table for incident electron energies upto 1.5 MeV. All computer code needed to duplicate these computations is available through the EMMPDL.

Introduction

For the last two decades, materials scientists have realized that the kinetic energy of a fast incident electron at high enough accelerating voltages is sufficient to displace atoms from their interatomic sites [1,2]. During this time high voltage electron microscopes (HVEM's) were routinely used to induce atomic displacement damage in materials as an aid to studying the mechanisms of radiation damage. For the most part, conventional TEM operating in the 100-200 kV regime were exempt from these effects in metallic systems, due in part to their low accelerating voltage

and relative poor vacuum environments. Recently, however, it has been shown that although the analytical electron microscope can be operated below the threshold for displacement damage to the bulk lattice, atomic displacement effects can give rise to preferential mass transport or loss in conventional 100-300 kV instruments [3,4].

Results and Discussion

Atomic sputtering by electrons results from knock-on momentum transfer from the incident electrons to atomic nuclei. This momentum transfer is a function of the incident electron energy, the atomic mass of the specimen, and the binding energy. The energy transfered (T_T) to an atom by a fast incident electron of mass m_O, is given by the expression [5]:

$$T_T = \frac{2 * T_O * (T_O + 2 * m_O c^2) * \sin^2(\frac{\phi}{2})}{M c^2} \quad (1.)$$

where T_O is the kinetic energy of the incident electron ($T_O = eV_O$, e=electronic charge & V_O= accelerating potential) , M is the mass of the nucleus and ϕ the direction of scattering (forward scattering direction being defined as $\phi = 180^O$). Beyond some critical threshold the energy transferred to the atoms within the solid is sufficient to permanently displace (T_d) an atom from its lattice site or sputter (T_s) it from the electron exit surface of the solid. It is at these threshold energies where electron damage becomes important to microanalysis. If the atoms in the solid are no longer constrained within the lattice and can become mobile then this process may result in a change of the local composition. In order to assess the point at which radiation damage manifests itself, it is necessary to determine values for both T_d and T_s. For some materials of interest experimental values of T_d exist. These have been reviewed recently by King etal [6]. However, since the value of T_d is not generally known for

all elements, we obtain estimates of both T_d and T_s, using the sublimination energy (T_{sub}) of a solid as a basis for estimation. As first suggested by Seitz and later confirmed by others, T_d is approximately 4-5 x T_{sub} [7,8]. Similiar relationships for T_s have not been established, however, it is reasonable to assume that its value should be in the range of $T_{sub} \leq T_s \leq 2\,T_{sub}$. Table 1 documents values of T_T, T_d, T_s, for various systems as a function of accelerating voltage. The values of T_d were taken from the literature [6,8] and in this case do to their strong dependance upon crystallographic direction the minimum values reported were used here. Those of T_s were based upon the simple relationship assumed above. As one can see from this table the proximity of the threshold for atomic sputtering in metallic systems to the accelerating voltages currently available in modern analytical microscopes demands further study.

In order to further assess the magnitude of this surface sputtering phenonmenon it is important to have estimates of the sputtering cross-sections by electrons. This sputtering process is expected to predominate in metallic systems in contrast to the desorption induced electron transitions (DIET) which rules in non-metallic specimens [9]. To calculate the sputtering cross-section the procedure developed by Oen [5] was followed, where we calculate the total cross-section σ_T for displacement by electrons using:

$$\sigma_T(T_o, T_d) = \int_{T_d}^{T_T} \frac{d\sigma}{dT}\, dT \qquad (2.)$$

where $d\sigma/dT$ is the relativisitic differential electron scattering cross-section for transfering an energy T to an atom by an electron of kinetic energy T_o for the process having a threshold energy T_d. The computations begin by first numerically evaluating the total Mott cross-section, from which the Rutherford differential cross-section is obtained. The quantity $d\sigma/dT$ is then integrated to obtain the total

displacement cross-section. The details of these calculations are available in an ANL-Technical Memorandum [10], and the corresponding computer code through the Electron Microscopy and Microanalysis Public Domain Library[11]. Calculations were performed on a DEC VAX 11/785 for all solid elements in the periodic table from threshold to 1.5 MeV. Threshold values of T_{sub} $2T_{sub}$, $4T_{sub}$, $5T_{sub}$ and where available experimentally determined values of Td were used in the calculations. The results of these calculations are summarized in extensive tables in the ANL Technical Memo, and are available upon request.

Figures 1 and 2 summarize fraction of these calculations by presenting the atomic sputtering cross-section as a function of atomic number for accelerating voltages of 100 , 300, and 1000 kV. In this calculation we have used the sputtering threshold energy $T_s=T_{sub}$ (Fig. 1) and $T_s=2T_{sub}$ (Fig. 2) which should bracket the surface sputtering regime. We observe that at 300 kV and higher a substantial number of elements have cross-sections which exceed 300 Barns. These levels are comparable to the typical x-ray production cross-sections, and thus for thin specimens one can approach the situation where mass loss during a typical x-ray analysis experiment may be significant, as has been experimentally observed [4]. Consider for example the following order of magnitude calculation: for a cross-section of 100 Barns , a 1 nm probe having a current density of $10^5 A/cm^2$ in a material whose atomic surface density is 10 atoms/nm^2, we calculate an atomic sputtering rate of ~500 atoms/sec at the exit surface of a thin TEM specimen.

Given this relatively high cross-section, one immediately asks the question as to why sputtering effects have not been reported extensively. Reference once again to Figure 1, shows that the sputtering cross-section for carbon is low. Hence, in instruments having poor vacuum systems the deposition of hydrocarbons on the surface will act as a barrier to sputtering inhibiting the process. The development of

clean, medium voltage UHV instruments may, therefore, open up a new set of problems for microanalysis.

In contrast we might also suggest that the electron sputtering process can lead to the development of a new microanalysis technique. Here, we consider the prospect that the sputtered (neutral) atoms leaving the exit surface of the specimen could be reionized by a tunable laser beam. These ions could then be subsequently extracted and analyzed using a conventional mass spectrometer. This has the potential of providing an extremely sensitive microanalysis technique, albeit a destructive one.

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Table 1
Comparison of Maximum Transferable Kinetic Energy to Selected
Elements with Displacement and Sputtering Energies
at 100, 200, 300 and 400 kV (all values in eV)

Element	<-----------T_T------------>				T_d[1]	T_s[2]
	(100kV	200kV	300kV	400kV		
Al	8.93	19.5	31.6	45.3	16	3.5-7.0
Ti	5.00	11.0	17.8	25.5	15	4.9-9.8
V	4.73	10.3	16.72	24.0	29	5.3-10.6
Cr	4.63	10.1	16.38	23.5	21	4.1-8.2
Fe	4.31	9.40	15.25	21.8	16	4.3-8.6
Co	4.08	8.91	14.45	20.7	23	4.4-8.8
Ni	4.10	8.94	14.5	20.8	21	4.5-9.0
Cu	3.79	8.26	13.4	19.2	18	3.5-7.0
Zn	3.69	8.03	13.03	18.7	16	1.4-2.8
Nb	2.59	5.65	9.17	13.2	24	7.5-15.0
Mo	2.51	5.47	8.88	12.7	27	6.8-13.6
Ag	2.23	4.87	7.90	11.3	28	3.0-6.0
Cd	2.14	4.67	7.58	10.9	20	1.2-2.4
Ta	1.33	2.90	4.71	6.75	33	8.1-16.2
Pt	1.23	2.69	4.37	6.26	33	5.9-11.8
Au	1.22	2.67	4.32	6.2	36	3.8-7.6

Notes:

1. T_d based upon experimentally measured values [ref 6,8]

2. T_s approximated using assumed relation $T_{sub} \leq T_s \leq 2T_{sub}$
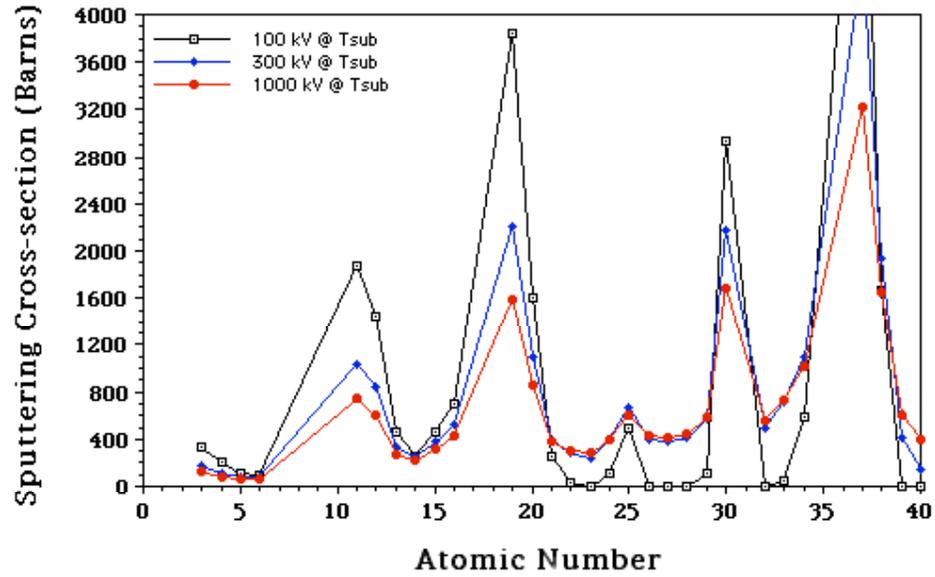
Figure Captions
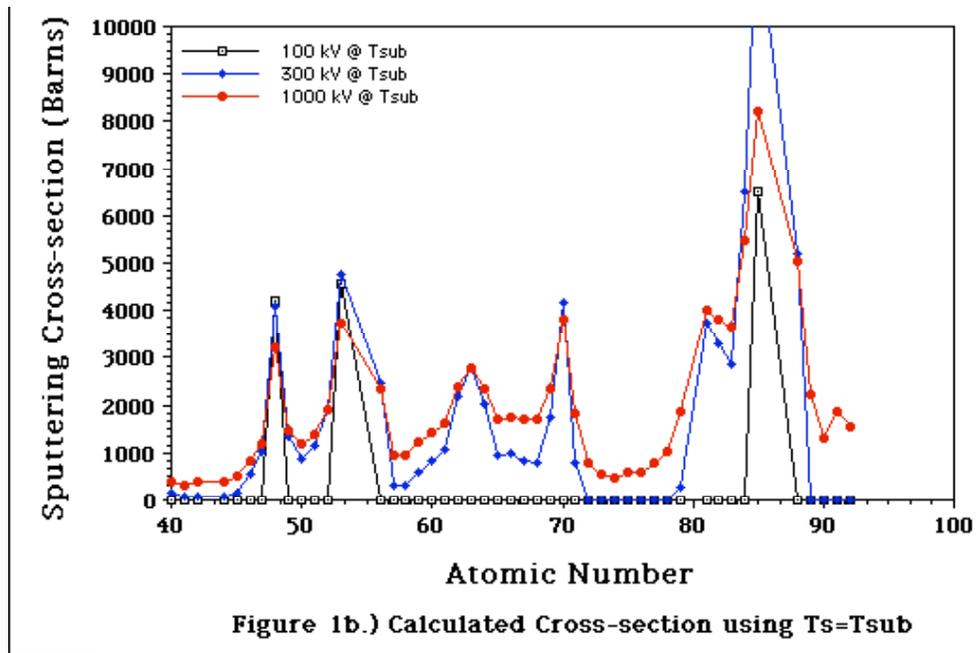
Figure 1a.) Calculated Cross-section using Ts=Tsub

Figure 1b.) Calculated Cross-section using Ts=Tsub

Figure 1. Calculated atomic sputtering cross-section as a function of atomic number for accelerating voltages of 100, 300 and 1000 kV using an assumed threshold energy for sputtering of $T_s = T_{sub}$.
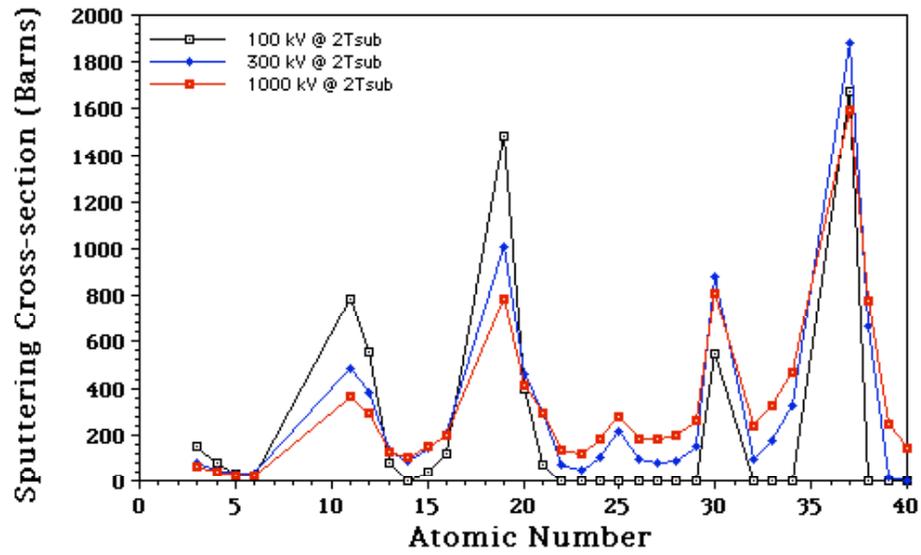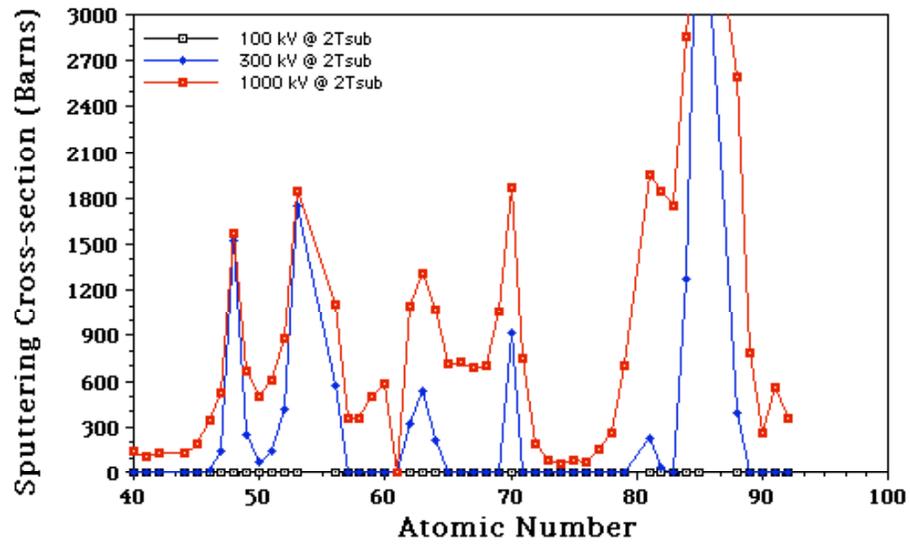
Figure 2a.) Calculated Cross-section using Ts=2Tsub

Figure 2b.) Calculated Cross-section using Ts=2Tsub

Figure 2. Calculated atomic sputtering cross-section as a function of atomic number for accelerating voltages of 100, 300 and 1000 kV using an assumed threshold energy for sputtering of $T_s = 2T_{sub}$.