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CALCULATED SPUTTERING AND ATOMIC DISPLACEMENT CROSS-SECTIONS FOR APPLICATIONS TO MEDIUM VOLTAGE ANALYTICAL ELECTRON MICROSCOPY*

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Calculated Sputtering and Atomic Displacement Cross-sections for Application to Medium Voltage Analytical Electron Microscopy

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The development of medium voltage electron microscopes having high brightness electron sources and ultra-high vacuum environments has been anticipated by the microscopy community now for several years. The advantages of such a configuration have been discussed to great lengths , while the potential disadvantages have for the most part been neglected. The most detrimental of these relative to microcharacterization are the effects of electron sputtering and atomic displacement to the local specimen composition. These effects have in the past been considered mainly in the high voltage electron microscope regime and generally were ignored in lower voltage instruments. Recent experimental measurements [1-6] have shown that the effects of electron sputtering as well as radiation induced segregation can be observed in conventional transmission electron microscopes. It is, therefore, important to determine at what point the effects will begin to manifest themselves in the new generation of medium voltage analytical electron microscopes. In this manuscript we present new calculations which allow the individual experimentalist to determine the potential threshold levels for a particuliar elemental system and thus avoid the dangers of introducing artifacts during microanalysis.

Discussion

Electron displacement damage occurs when kinetic energy is transferred from the electrons in the incident probe to the atoms of the sample[7,8]. If the energy transferred is sufficient, atoms may be displaced from their lattice sites; either to form point defects, which may subsequently migrate and cause elemental rearrangement, or they can be sputtered from the specimen. In either case, the amount of kinetic energy (T_T) transferred from an incoming electron (mass m_0) to the nucleus of a specimen atom depends upon the kinetic energy of the electron ($T_T=eV_0$, e=electronic charge & V_0= accelerating potential) , the mass of the nucleus (M) and the direction of scattering (ϕ) and can be written[9-11]:

$$T_T=[2*T_E*(T_E+2*m_0c^2)*\sin^2(\phi/2)]/[Mc^2] \quad 1.$$

with the forward scattering direction defined as $\phi=180^o$.

Beyond some critical energy 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

surface of the solid. It is this point at which electron damage becomes important to microanalysis since the atoms in the solid no longer are constrained within the lattice and can become mobile or are completely removed from the specimen, thus changing the local composition. In order to assess the point at which radiation damage manifests itself, it is necessary to determine values for T_d and T_s. Experimental determinations of the displacement threshold energy T_d have been reviewed recently [9], however the data base is limited. Further complicating the problem is the fact that T_d is a function of crystallographic direction. In FCC metals, for example, the lowest energy directions tend to lie along the <110> while the highest energy are generally perpendicular to the <111>. In BCC metals the lowest energy directions tend to be <100> and <111> generally the highest. In HCP materials there is little data available and no clear systematic trends have been reported.

Seitz [10] has suggested that T_d should be directly related to the sublimation energy (T_{sub}) of an element by a multiplicative factor of 4 or 5. In figure 1 we compare the values of the mean sublimation energy T_{sub} as a function of atomic number with experimentally determined values of T_d divided by a factor a 5. As one can see there is a good correlation between the relationship of $T_d \sim 4\text{-}5*T_{sub}$.. In this data set, only those T_d values corresponding to the lowest energy directions are plotted, since the sublimation energy will reflect this rather than any orientation dependence.

In sputtering, we are concerned with the removal of atoms from the electron exit surface of the specimen. Since the atoms at the surfaces are not totally surrounded by other atoms, the energy required to sputter them is necessarily less than that required to displace them to form defects within the solid; but not less than that required to sublime an atom from the surface. As an upper limit one can therefore estimate that $T_s \sim 2T_{sub}$.

By combining the relationships of sublimination, sputtering and displacement energy thresholds and using equation 1, one can calculate as a function of atomic number the minimum accelerating voltage at which one would expect to observe the onset of either sputtering or atomic displacement in a *contamination free environment*. The results of this calculation are plotted in figure 2, where we plot the minimum accelerating voltage (V_{min}) necessary to transter $T_s=2*T_{sub}$ and $T_d= 5*T_{sub}$ eV of energy. The important point to note in this figure is that the onset values for many elements for both sputtering and displacement is less than 400 kV.

Now that we have established a systematic set of values for of T_s, and T_d, albeit they are estimated, we can proceed to evaluate the cross-section for electron sputtering and atomic displacement. In 1973, Oen [11] published tables of calculated cross-sections for atomic displacement by electrons as a function of electron energy for 37 selected elements. Although this was a major undertaking it was, in the main, directed toward application to high energy electron accelerators, operating in the tens to hundreds of MeV regime. Thus, much of the data presented in his tables is inappropriate for general usage by the electron microscopy community. We have undertaken the task of expanding upon Oen's work with the specific intent of providing a

systematic set of calculations relevant to the electron microscope environment.

Atomic displacement cross-section calculations have been carried out systematically as a function of atomic number for accelerating voltages up to 1.5 MeV. Threshold energies of T_{sub}, $2T_{sub}$, $4T_{sub}$ and $5\,T_{sub}$ were assumed and the calculation procedure was essentially the same as outlined by Oen. Comparision of duplicate calculations with Oen's work indicate a maximum error of 0.5% relative to his results. When the completed the results of these new calculations as well as the complete computer code used to perform the computations will be the subject of a special ANL Technical Memo to be issued during the next year; in addition, the source code will be made available to the scientific community through the EMMPDL [12]. The calculations completed to date are summarized graphically in figure 3, for the elements Li, Be, B, C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Ge,Y, Zr, Nb, and Mo. Sputtering cross-sections were calculated using the estimated threshold energy $T_s=2T_{sub}$, while displacement cross-sections were evaluated at $T_d=4T_{sub}$.

Concluding Remarks

The results of this study allow the experimentalist to determine prior to microanalysis whether one needs to consider the with complications to an analysis due to sputtering or displacement damage. These cross-section calculations can be combined with related calculations of the x-ray or electron energy loss generation/detection rates for a given set of experimental conditions to determine, if conditions can be such that the specimen composition may change during the course of an experimental measurement. [1,2] This work was supported by the U.S. Depart. of Energy at Argonne National Laboratory under contract #BES-Mat. Sci. W-31-109-Eng-38.

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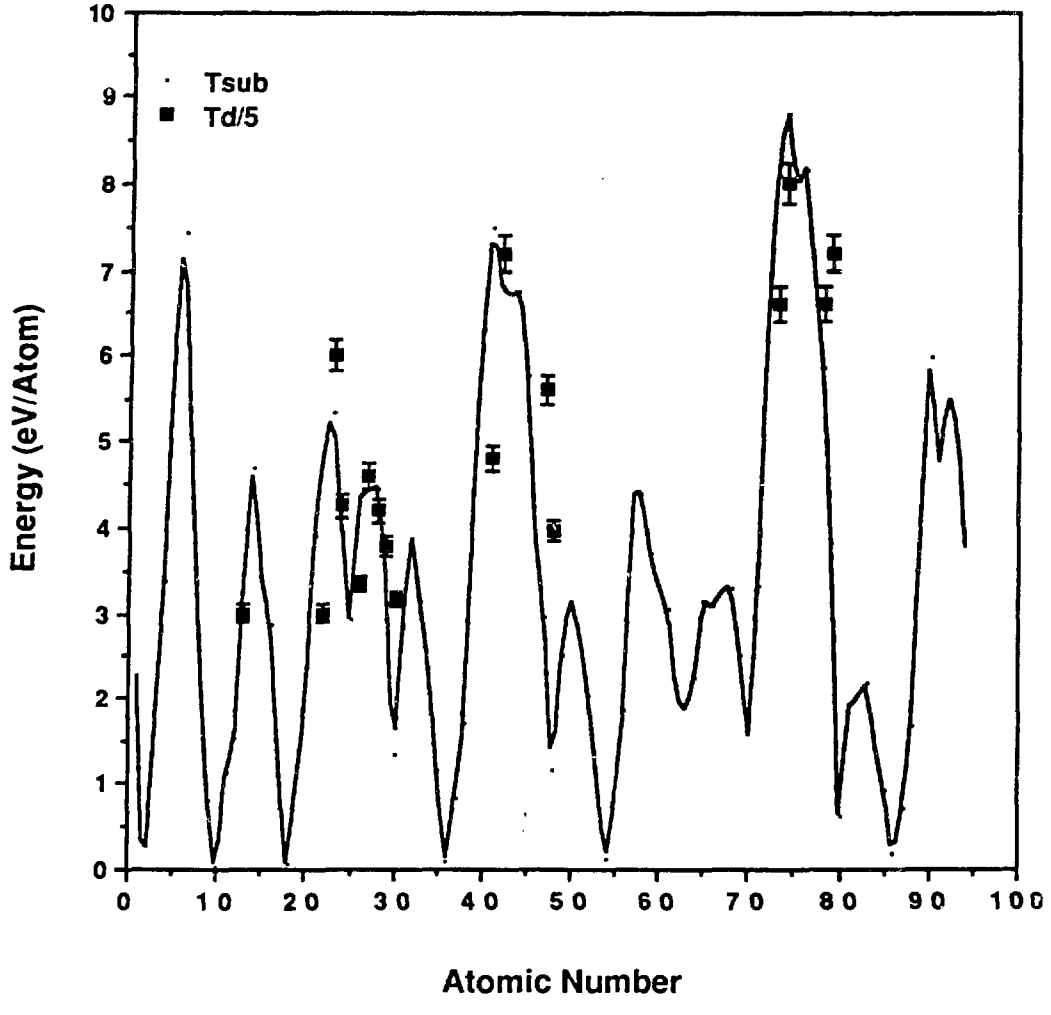
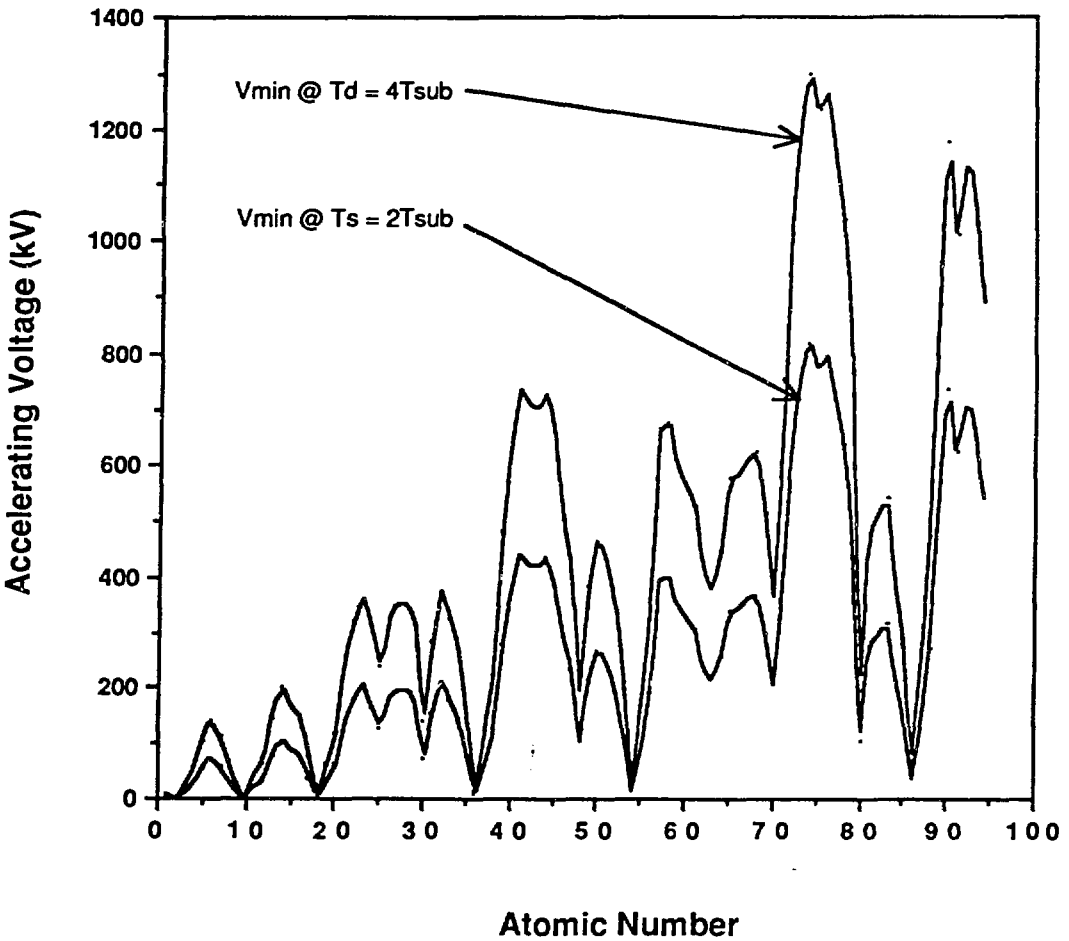
Figure Captions

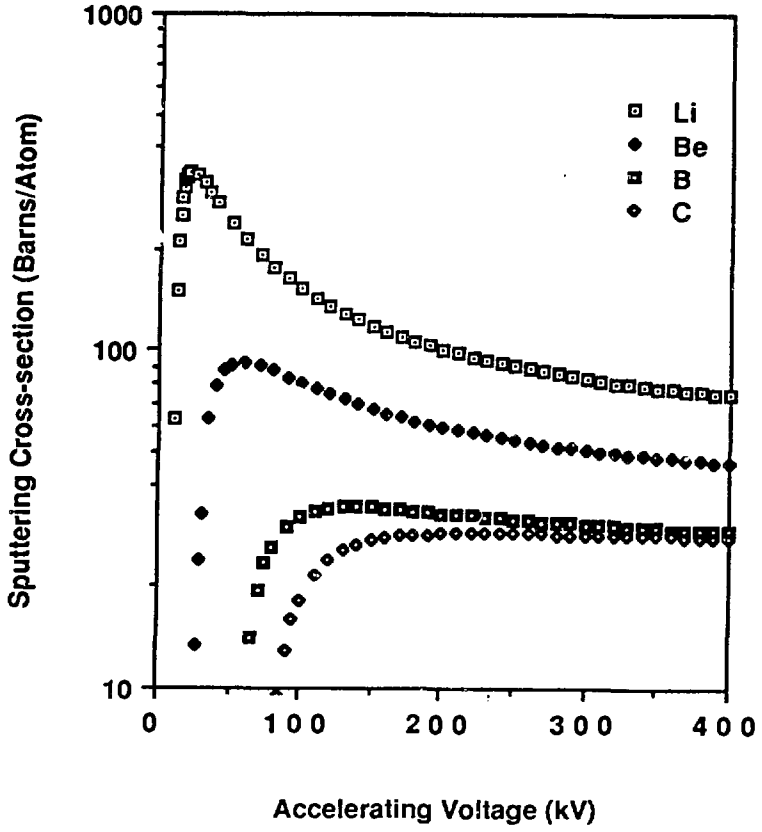
Figure 1. Comparison of the sublimination energy (T_{sub}) with one fifth of the experimentally determined displacement energies ($T_d/5$) as a function of atomic number.

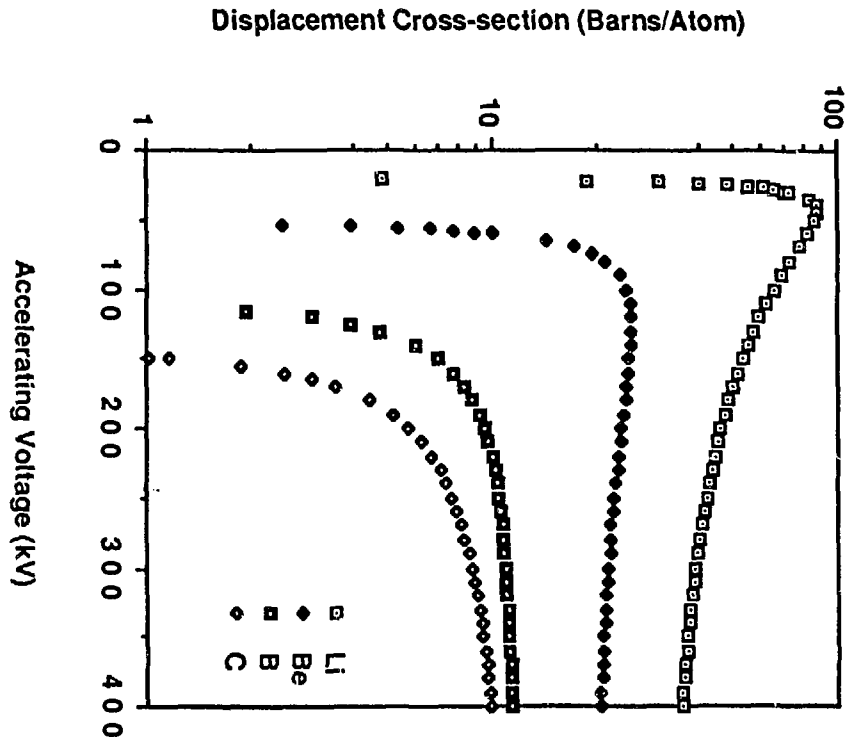
Figure 2. Calculated minimum voltages (V_{min}) for the onset of electron sputtering ($T_s=2T_{sub}$) and atomic displacement ($T_d=4T_{sub}$).

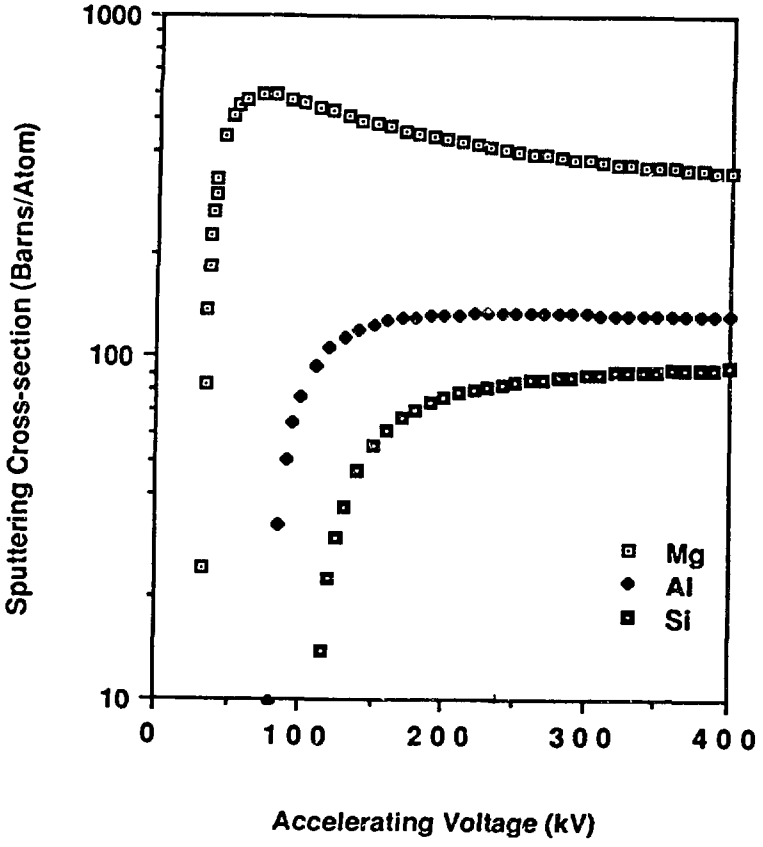
Figure 3. Calculated cross-sections for sputtering ($T_s=2T_{sub}$) and atomic displacement ($T_d=4T_{sub}$) as a function of accelerating voltage for the elements Li, Be, B, C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Ge, Y, Zr, Nb, and Mo

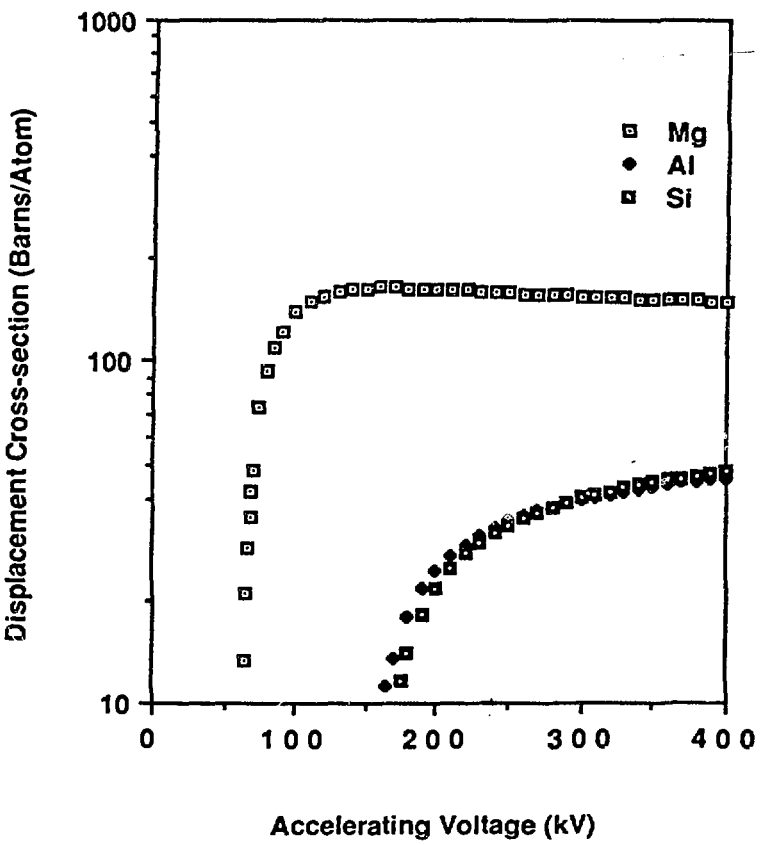

Tsub
Td/5
Energy (eV/Atom)
Atomic Number
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100

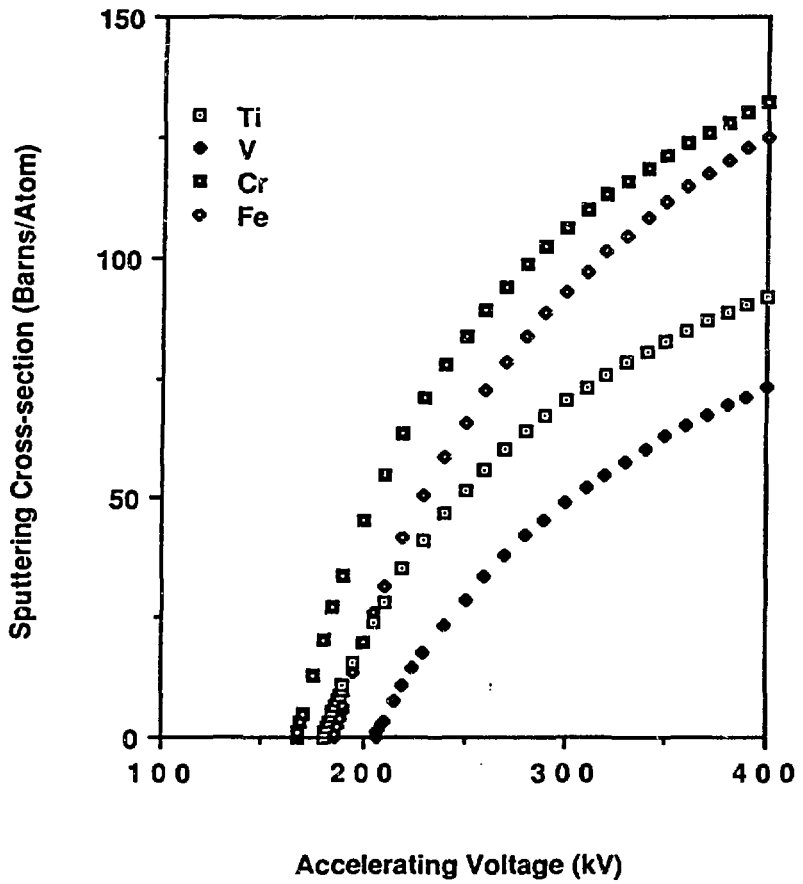

Vmin @ Td = 4Tsub
Vmin @ Ts = 2Tsub
Accelerating Voltage (kV)
Atomic Number
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60
70
80
90
100

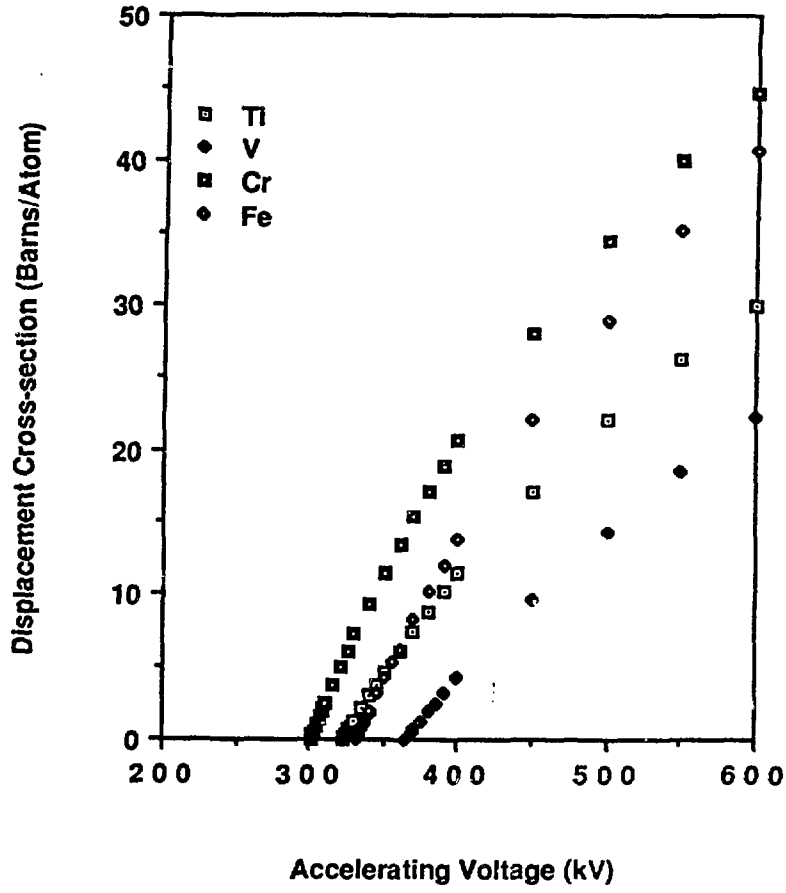

1000
100
10
0
100
200
300
400
Li
Be
B
C
Sputtering Cross-section (Barns/Atom)
Accelerating Voltage (kV)

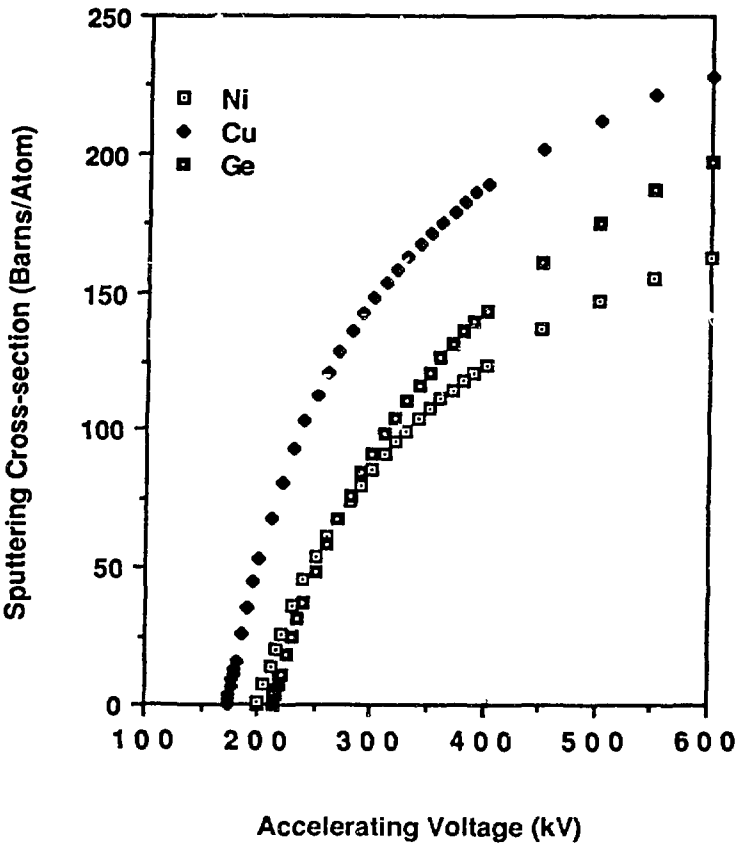

Displacement Cross-section (Barns/Atom)
1
10
100
0
100
200
300
400
Accelerating Voltage (kV)
Li
Be
B
C

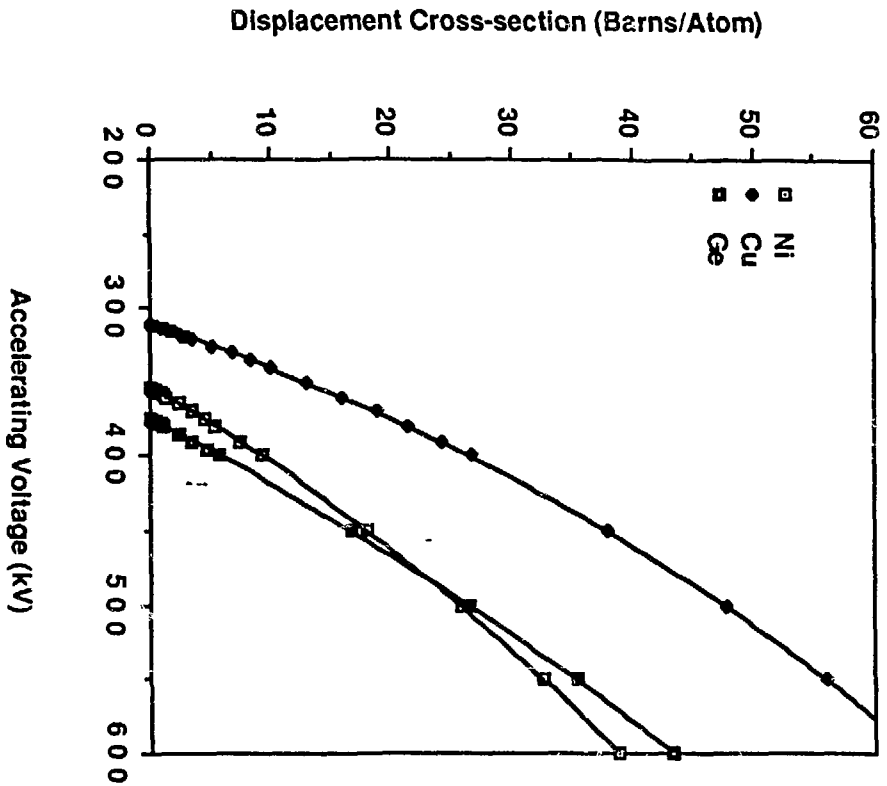

1000
100
10
Sputtering Cross-section (Barns/Atom)
0
100
200
300
400
Accelerating Voltage (kV)
Mg
Al
Si

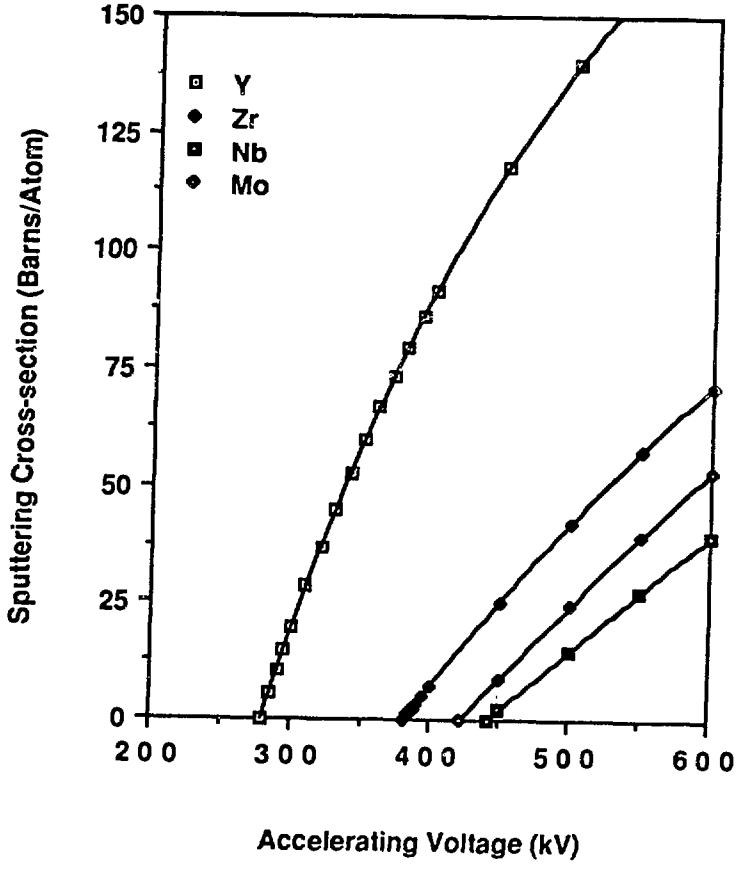

1000
100
10
0
100
200
300
400
Mg
Al
Si
Displacement Cross-section (Barns/Atom)
Accelerating Voltage (kV)

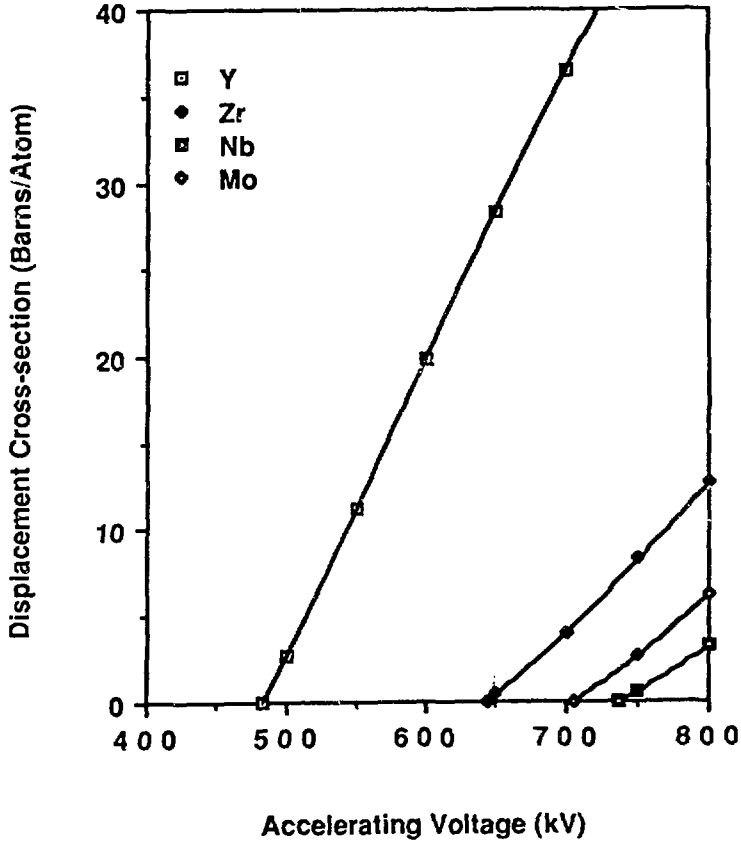

150
100
50
0
100
200
300
400
Ti
V
Cr
Fe
Sputtering Cross-section (Barns/Atom)
Accelerating Voltage (kV)


Displacement Cross-section (Barns/Atom)
50
40
30
20
10
0
200
300
400
500
600
Ti
V
Cr
Fe
Accelerating Voltage (kV)


Sputtering Cross-section (Barns/Atom)
250
200
150
100
50
0
Ni
Cu
Ge
100
200
300
400
500
600
Accelerating Voltage (kV)


Displacement Cross-section (Barns/Atom)
0
10
20
30
40
50
60
200
300
400
500
600
Accelerating Voltage (kV)
Ni
Cu
Ge


150
125
100
75
50
25
0
200
300
400
500
600
Y
Zr
Nb
Mo
Sputtering Cross-section (Barns/Atom)
Accelerating Voltage (kV)


Displacement Cross-section (Barns/Atom)
40
30
20
10
0
Y
Zr
Nb
Mo
400
500
600
700
800
Accelerating Voltage (kV)