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DEPTH OF ORIGIN OF SPUTTERED ATOMS: EXPERIMENTAL AND THEORETICAL STUDY OF Cu/Ru(0001)*

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The depth of origin of sputtered atoms is a subject of considerable interest. The surface sensitivity of analytical techniques such as Secondary Ion Mass Spectrometry (SIMS) and Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA), and the sputtering properties of strongly segregating alloy systems, are critically dependent on the sputtering depth of origin. A significant discrepancy exists between the predictions of the Sigmund theory and computer sputtering models; in general, the computer models predict a much shallower depth of origin. The existing experimental evidence suggests that most of the sputtered atoms originate in the topmost atomic layer, but until recently, the results have not been definitive. We have experimentally determined the depth of origin of atoms sputtered from surfaces consisting of Cu films of less than two monlayers on a Ru(0001) substrate. The Cu/Ru target was statically sputtered using 3.6 keV Ar^+. The sputtered neutrals were non-resonantly laser ionized and detected using SARISA. The Cu/Ru sputtering yield ratio and the suppression of the Ru sputtering yield were determined for various Cu coverages. The results indicate that the majority of the sputtered atoms originate in the topmost atomic layer. The Cu/Ru system is also modeled using a modified TRansport of Ions in Matter (TRIM) code. It was found that TRIM C does not correctly treat the first atomic layer, resulting in a serious underestimate of the number of sputtered atoms which originate in this layer. The corrected version adequately describes the results, predicting that for the experimental conditions roughly two-thirds of the sputtered atoms originate in the first atomic layer. These results are significantly greater than the Sigmund theory estimate of >40%.

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DISCLAIMER

1. Introduction

Energetic ion bombardment of a target surface can, following a series of atomic collisions, lead to the ejection of target atoms. A fundamental understanding of this process, known as sputtering, is technologically important to a wide variety of industries. In the semiconductor industry, for instance, sputtering is used to create structured device surfaces both by deposition of sputtered atoms (sputter-deposition) and by removal of surface atoms (plasma etching). For magnetic confinement fusion, the sputtering process due to plasma-wall interactions represents the start of a parasitic energy loss mechanism which could unfavorably alter the input energy required to reach the scientific breakeven point. Furthermore, analytical instruments which utilize ion beam probes to detect sputtered atoms yield more information if the sampling depth of sputtering is well known.

Despite the importance of sputtering, a fundamental understanding of many aspects of this process has remained lacking. This is due both to the complexity of a sputtering event and to the experimental difficulties involved in its study. The depth of origin (D_o) of sputtered species is one such aspect which is currently the object of considerable debate. Theoretical efforts to understand the depth of origin of sputtered atoms are summarized in Table 1. Sigmund's theory,[1-3] based on an isotropic binary collision approximation, is analytic and defines two types of depths of origin. The first, called the characteristic D_o, is the depth from which 1/3 of all sputtered species are ejected. Implicit in this model is the assertion that the sputtering yield decreases exponentially with depth. While the D_o varies with target density this model typically predicts that 40% of all sputtered species originate in the surface atomic layer. A second definition of D_o is the sample thickness which gives rise to sputtering. While this number is target and primary ion dependent, for 5 keV Ar^+ normally incident on Cu, the depth contributing to the sputter yield is roughly 20 Å.

A second type of theoretical investigation is represented by computer simulations of the sputtering process. Two such efforts are represented by the Monte Carlo collision codes TRIM[4] and MARLOWE.[5,6] TRIM assumes an amorphous target and MARLOWE can utilize single crystal targets. A third computer code allows for multiple interactions by calculating multiple collisions in a crystal lattice.[7,8] As illustrated in Table 1, each of these calculations finds that greater than 75% of all sputtered atoms originate in the first atomic layer for a wide range of target, primary ion combinations.

Dumke and Tombrello[9] studied the sputtering of the liquid indium-gallium eutectic alloy using a 15 and 25 keV Ar^+ beam. Due to surface segregation, the concentration of indium at the surface was found to be greater than 94% as determined by Ion Scattering Spectroscopy (ISS) and Auger studies. The bulk indium concentration is only 16.5% in the eutectic alloy. By assuming that the second layer concentration was that of the bulk alloy and using a plate to collect the sputtered species, the experimenters determined that more than 85% of the sputtered species originated in the first layer for 15 keV ion bombardment. For 25 keV ion bombardment, the first layer contributed 70% of the sputtered atoms. If the assumption that only the very first layer concentration is affected by the surface segregation is incorrect, the estimates of the first layer contributions to the sputtering yield are also incorrect.

Definitive experimental studies of D_o are virtually nonexistent. The difficulty arises in producing a well-characterized layered structure and then *quantitatively* measuring the sputtering yields of each layer component with a primary ion dose low enough to avoid residual damage effects.

In this publication, Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA)[10-13] is used to investigate D_o for solid surfaces. The method of investigation is straightforward. First, a well-characterized Cu overlayer is deposited upon a clean single crystal Ru surface (0001). Then SARISA is used in a nonresonant ionization mode to simultaneously determine the sputtering yield of both Cu and Ru, S_{Cu} and S_{Ru}. By quantitatively detecting S_{Cu} and S_{Ru} as a function of Cu coverage, the suppression of the Ru yield and the ratio of sputtered Cu to Ru can be determined. Subsequent experiments have determined that the secondary ion yields for this system represent a negligible fraction of the sputtered flux. Because of the high detection efficiency of the SARISA technique, these measurements are made in a *static* mode, i.e., on average over the course of measurement no primary ion strikes a previously impacted area.

There are several important reasons that the extensively studied Cu/Ru(0001) system has been chosen for this work. Deposition of Cu on the Ru(0001) surface has been demonstrated to result in layer by layer Cu film growth up to 2 monolayer coverage.[15-20] Furthermore, this growth is essentially pinhole free[20] with the first layer being more strongly bound to the surface than the second Cu layer.[15-20] LEED patterns as a function of Cu coverage demonstrate pseudomorphic growth for up to 2 monolayers of Cu coverage.[16-19]

In this publication, we will briefly describe Auger Electron Spectroscopy (AES) of this surface which confirms the previous work and allows unequivocal establishment of the absolute Cu coverage. This is extremely important since a careful measure of the D_0 for sputtered atoms on this system hinges on precise determination of the Cu coverage for each sample.

In conjunction with the experiments, model calculations have been made using a corrected version of the TRIM Monte Carlo code, based on the Biersack-Ziegler universal potential. The basic approach has been described elsewhere[24], but the correction used in the present work will be briefly described. TRIM treats the electronic and nuclear losses independently. The electronic losses are treated as a continuous process beginning when the primary ion crosses the surface in accord with LSS theory. The nuclear losses occur only when a collision occurs between the cascade atoms and the stationary lattice atoms. It is assumed by TRIM that a cascade atom must travel at least a distance P_{max} between consecutive nuclear collisions, where P_{max} is proportional to the average interatomic spacing. For the first collision however, the distance is measured from the surface of the material. Since P_{max} is typically 1-2 Å, a significant fraction of the nuclear stopping in the first atomic layer is ignored, and the sputtering yield associated with atoms originating in the first atomic layer is underestimated. This unphysical result is evident in depth of origin calculations using TRIM[24] in which no sputtered atoms were found to originate in the first atomic layer. This artifact is not present in an earlier version of TRIM[25,26] which treats the electronic stopping as a discrete process and therefore defines the surface in a consistent manner. As a simple cure, P_{max} has been calculated and the first atomic layer has been increased in thickness by P_{max}. All of the nuclear collision events are therefore correctly counted, although there is an increased electronic energy loss corresponding to the transit through the first 1-2 Å of material. Consequently, the available kinetic energy is slightly reduced when the primary ion reaches the "true surface". An estimate of the effect of this approximation may be made from Fig. 1, which shows the calculated first and second layer depth of origin for Ar^+ bombardment of Ru as a function of primary ion kinetic energy. For low energies, the depth of origin increases rapidly with kinetic energy, but for energies in excess of 1-2 keV, the depth of origin is nearly independent of the primary energy. Consequently, the error introduced by artificially redefining the surface is only expected to be significant at very low impact energies and is not expected to affect the application to the current experimental conditions.

2. Experimental

The SARISA apparatus consists of four parts: a UHV chamber, two pulsed lasers, a pulsed ion source, and an ion detector. The UHV chamber is equipped with LEED (VG Corporation), a single pass cylindrical mirror electron energy analyzer for Auger spectroscopy (Physical Electronics Corporation Model 150), and a quadrupole residual gas analyzer (UTI model 100C). The chamber is routinely pumped into the low 10^{-10} torr range by a 200 l/s ion pump (Ultek model 207-0232) assisted by a titanium sublimator. During ion bombardment the chamber pressure rises into the low 10^{-9} torr region, with argon as the primary residual gas. The laser used for non-resonant ionization is a XeCl excimer laser (Lambda Physik, EMG 201 MSC) which provides a 10 nsec, 300 mj pulse at 308 nm (4.03 eV). With ionization potentials of 7.72 eV and 7.36 eV for copper and ruthenium respectively, both ionizations require two photons.

A diagram of the SARISA apparatus is shown in figure 2. A complete description of the operation of the SARISA apparatus is given in references 10-13. The 5 keV argon ion beam is produced by an ion source (Colutron Corporation). The beam is apertured to 10 namps and then chopped into 500 nsec pulses. The beam diameter at the target was approximately 30 microns and each pulse contains approximately 3.1×10^4 argon ions. The laser pulse ionizes the sputtered neutrals above the target surface. An Energy and Angular Refocussing-Time of Flight (EAR - TOF) mass spectrometer is used to separate and detect the different photo-ion species.

The ruthenium single crystal (Metal Crystals and Oxides, LTD) was oriented and cut perpendicular to the (0001) axis. The (0001) face was oriented to $\pm 1^o$ and polished to a mirror finish. A commercially available heater button (Spectra-Mat Corp.) was used to heat the sample to temperatures of up to 1500K. Good thermal contact was made between the heater button and the crystal by bonding the crystal to the heater with a high temperature alumina based adhesive (Cotronics Corporation).

Auger spectroscopy was used to monitor the cleanliness of the ruthenium surface. Cleaning was achieved by Ar^+ bombardment followed by repeated cycles of heating the crystal to 1500K in a 5×10^{-7} torr oxygen background and then heating the crystal to 1500K in vacuum.[14,19,20] The Auger spectrum showed no traces of sulphur or oxygen. The carbon Auger feature near 274eV is of nearly the same energy as the ruthenium structure near 274eV. A carbon free surface is assumed if the differentiated negative to positive peak ratio of the ruthenium 274eV auger feature is 1.20.[14,19,20]

Copper was deposited onto the ruthenium by evaporation. Marz grade copper wire was wrapped around a tungsten filament and the tungsten filament was mounted on outgassing loops. By controlling the voltage across the deposition filament, reproducible copper evaporation rates can be achieved.[14,19,20] The deposition filament was outgassed for several hours before use; Auger revealed no contaminants in the deposited copper layer, except for chlorine. The chlorine was removed by annealing the sample at 1100K for about five minutes.

The calibration of the copper coverage was carried out in a unique fashion. Copper was slowly and in a controlled manner evaporated from the ruthenium surface. The target was positioned in front of the Auger spectrometer and the differentiated peak to peak intensities of the Copper 920eV and 60eV and the ruthenium 274eV were recorded for decreasing copper coverages. A 3 keV, 5 microamp electron beam was used and the modulation voltage was 2 eV. Neither the sample position nor the Auger parameters were changed for the course of the experiment. This allowed the absolute copper and ruthenium Auger intensities to be compared directly. As expected, a plot of the copper vs. the ruthenium Auger intensities was linear within copper overlayers and showed sharp breaks at the completion of one monolayer.[15-18,21,22] Furthermore, the increased binding energy of the first copper layer relative to that of the second layer was expected to show a dramatic change in the copper desorption rate. With sufficient control of the desorption, the change in the Auger intensities of copper and ruthenium with heating time showed a dramatic change when only one monolayer of copper remained.

3. Results and Conclusions

The results of the sputtering experiment are shown in figure 3. Three measurements of the Cu/Ru Sputter yield ratio, S_{Cu}/S_{Ru}, for three different copper coverages were completed. As expected, the experimental results show that as more copper is deposited, S_{Cu}/S_{Ru} increases. At one monolayer of copper coverage, S_{Cu}/S_{Ru} is 3.2. This is significantly larger than the ratio of the elemental Cu sputtering yield, $S_{Cu,tot}$, to the elemental Ru sputtering yield, $S_{Ru,tot}$, of 1.67[23], illustrating the large surface contribution to sputtering.

The experimental value of S_{Cu}/S_{Ru} may be used to estimate the first layer contribution to sputtering, ie., the suppression of the Ru sputtering yield. Assuming that the fraction of the total elemental sputtering yield originating in the topmost layer is the same for both Cu and Ru and that the Cu and Ru atoms sputter from the Cu/Ru system as if from their respective bulk metals, then:

$$S_{Cu}/S_{Ru} = X\, S_{Cu,tot} \,/\, (1-X)\, S_{Ru,tot}$$

where X is the fraction of the total sputtering originating in the first layer, (1-X) is the fraction arising from below the first layer, and $S_{Cu,tot}$ and $S_{Ru,tot}$ are the elemental sputter yields for Cu and Ru. For 3.6 keV Ar^+ bombardment, $S_{Cu,tot}$ and $S_{Ru,tot}$ are 4.5 and 2.7, respectively .[23] Substituting the experimental value of 3.2 for S_{Cu}/S_{Ru} into the equation, X is calculated to be .66, ie., two thirds of the sputtering yield is from the first layer.

In order to assess this value let us examine the critical assumptions. Similar first layer contributions to sputtering for Cu and Ru elemental targets are supported by TRIM calculations which show virtually identical depth of origin distributions for the sputtering of elemental Cu and Ru; 79 ± 4 % of the sputtering is from the first layer for both Cu and Ru. The assumption that Cu and Ru sputter with yields per layer similar to their bulk metals *underestimates* X since Cu is less effective in shielding the Ru substrate than is a layer of Ru. This is due to the mass mismatch between Cu and Ru, the lower binding energy of Cu to Ru than of Ru to Ru, and the decreased density of the Cu overlayer. TRIM calculations support this assertion. The suppression of the Ru sputter yield by one ML of Cu, calculated by TRIM, is 70 ± 4 %, while the calculated fraction of the total sputtering yield from the first layer of pure Ru is 79 ± 4 %. For these reasons, the Cu/Ru measurements are expected to be an *underestimate* of the first layer contribution to sputtering when compared with elemental targets.

Results of the TRIM computer calculations are also shown in figure 3. TRIM calculations of S_{Cu}/S_{Ru} increase with increasing Cu coverage, although more rapidly than do the experimental values. At one ML of Cu coverage, TRIM predicts a S_{Cu}/S_{Ru} of 4.5, a value somewhat higher than the experimental value of 3.2. TRIM predicts the suppression of the Ru sputtering yield due to one Cu monolayer to be 70%, in excellent agreement with the experimental estimate.

For the first time, definitive measurements on the depth of origin have been made. The studies were conducted on carefully characterized Cu covered Ru single crystals. The experimental results show that for 3.6 keV Ar^+ bombardment of the Cu/Ru system, sputtering is mostly a first layer phenomenon. Because the Cu overlayer is less effective in shielding the Ru substrate than is a layer of Ru, the first layer contribution to sputtering for the Cu/Ru system is expected to be less than that of pure Ru. For similar reasons, the depth of origin of sputtered atoms from many elemental targets may be at least as shallow as the Cu/Ru experiment indicates. Sigmund's analytical calculation of $X = 0.4$[1-3] is less than the experimental value of two-thirds. The TRIM results, showing much better although not exact agreement with the experiment, calculate the slightly higher value of 70%.

TABLE I. VARIOUS ESTIMATES OF THE DEPTH OF ORIGIN

SOURCE	DEFINITION	SPUTTERED FRACTION ARISING FROM FIRST LAYER
Sigmund (theory)[1-3]	Characterisic depth of Origin $D_O = 3/(4NC_O)$ N = Target Number Density C_O = constant (1.808)	< 40%
Sigmund (theory)[1-3]	Total thickness contributing to Sputtering is 25-50% of the Primary Ion Penetration Depth	N/A
TRIM[4] MARLOWE[5,6]	Binary Collision, Monte Carlo Computer Calculation	> 75%
MULTIPLE INTERACTION SIMULATION[7,8]		> 85%
In-Ga Liquid Eutectic (Experimental)[9]		>85%

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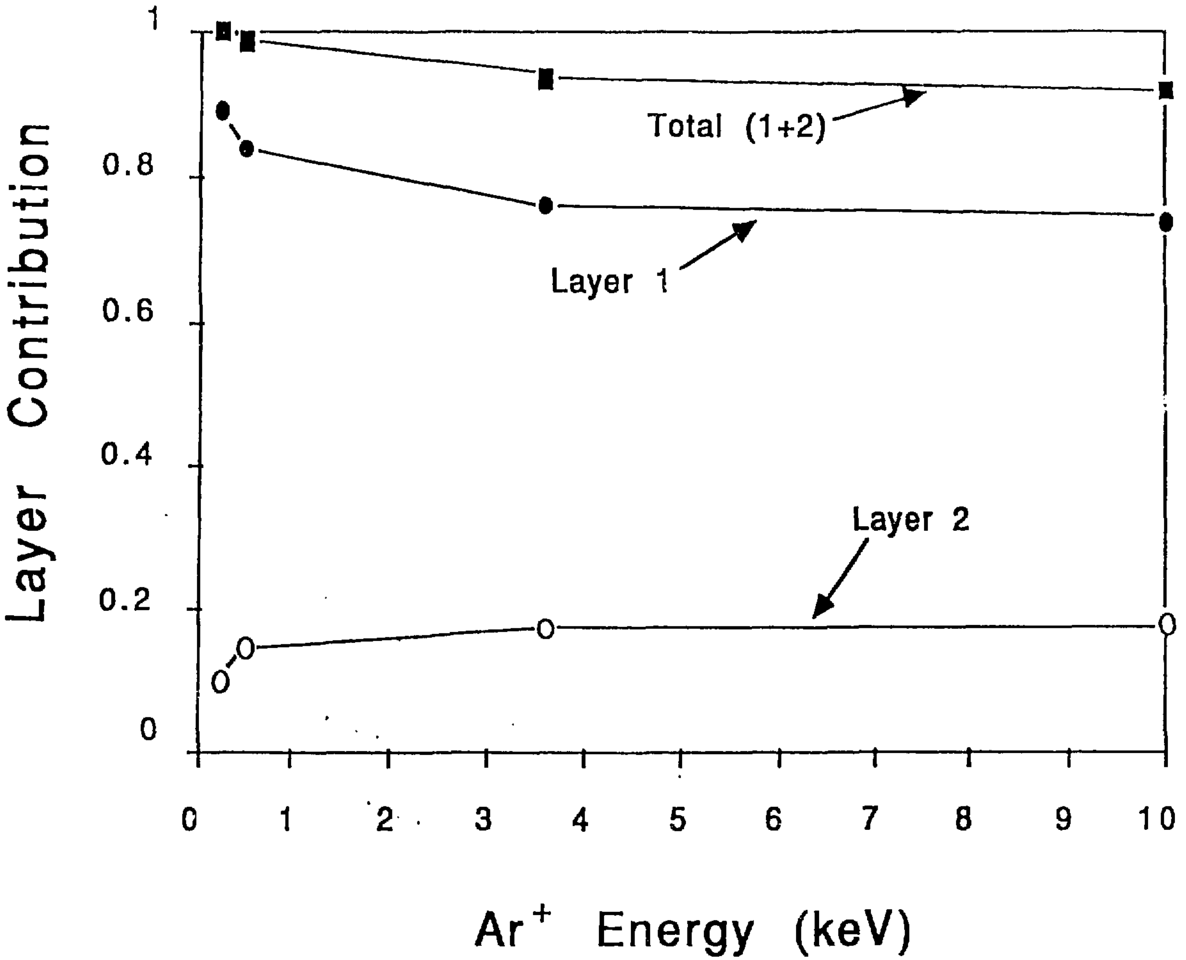
Figure Captions

Figure 1. A plot of the TRIM calculation of the first and second layer contributions to the total sputtering yield for Ru as a function of primary ion kinetic energy. Note that for primary ion energies of greater than 1-2 keV, the layer contributions to the depth of origin are nearly independent of the energy.

Figure 2. The SARISA apparatus.

Figure 3. A plot of the Cu/Ru sputtering yield ratio, S_{Cu}/S_{Ru}, versus Cu coverage in monolayers for both the experiment and the TRIM calculations. For both the experiment and the calculation, a 3.6 keV Ar^+ beam was used.


Layer Contribution
1
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
7
8
9
10
Ar$^+$ Energy (keV)
Total (1+2)
Layer 1
Layer 2

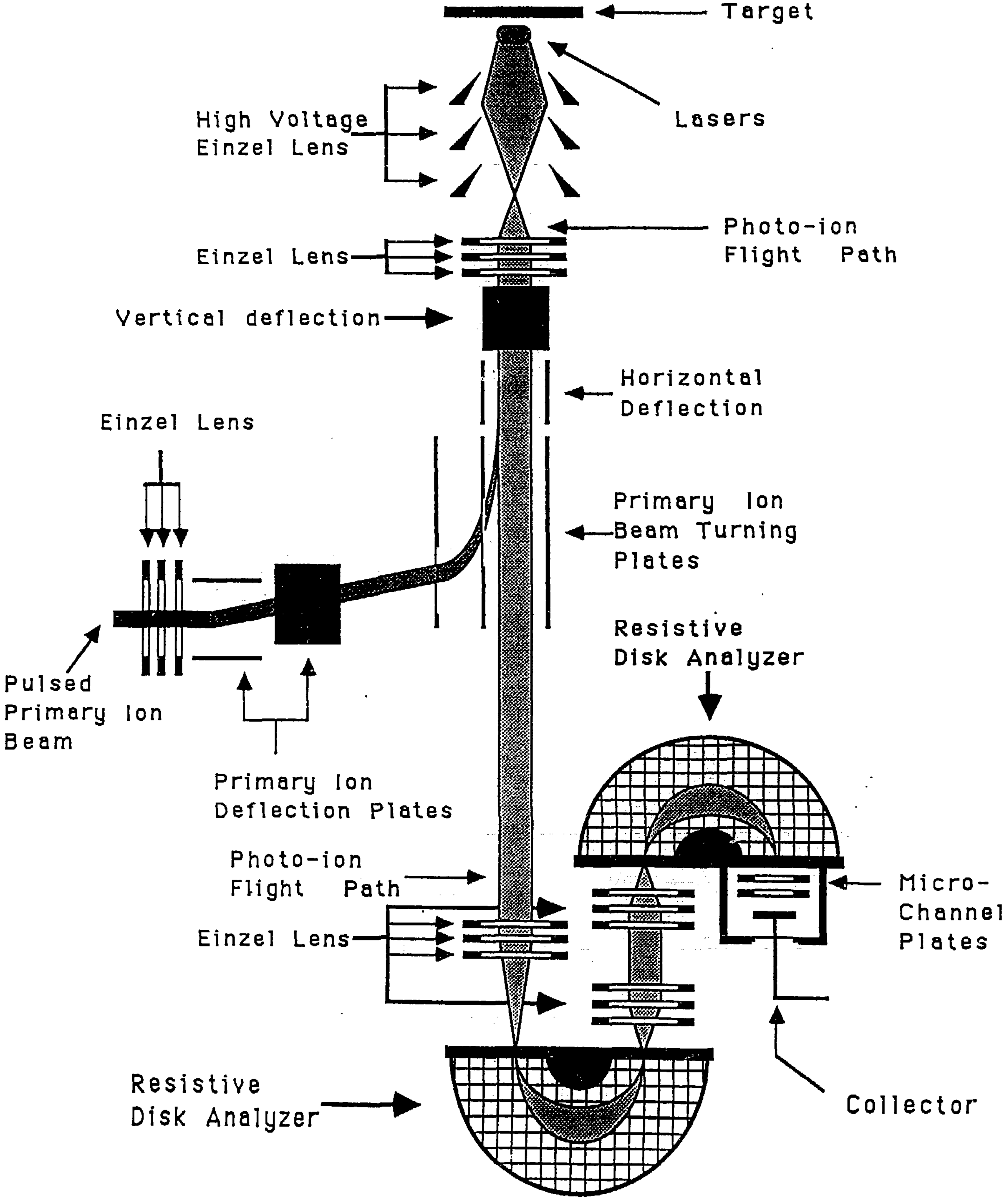
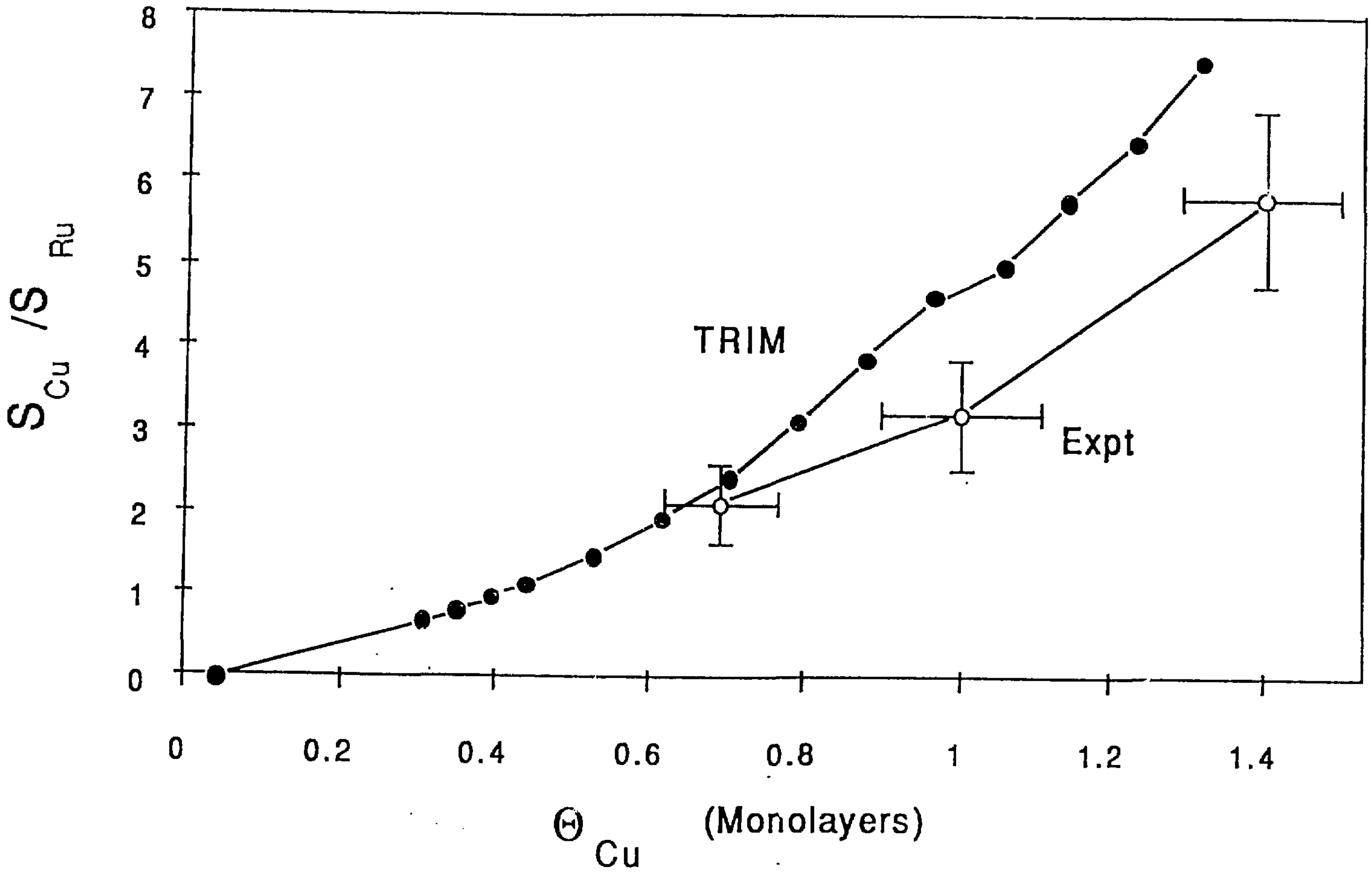


Figure 2. The SARISA apparatus.


8
7
6
5
4
3
2
1
0
S_{Cu} /S_{Ru}
TRIM
Expt
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Θ_{Cu} (Monolayers)