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PHOTON EMISSION PRODUCED BY PARTICLE-SURFACE COLLISIONS

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ABSTRACT

Visible, ultraviolet, and infrared optical emission results from low-energy (20 eV–10 keV) particle-surface collisions. Several distinct kinds of collision induced optical radiation are discussed which provide fundamental information on particle-solid collision processes. Line radiation arises from excited states of sputtered surface constituents and backscattered beam particles. This radiation uniquely identifies the quantum state of sputtered or reflected particles, provides a method for identifying neutral atoms sputtered from the surface, and serves as the basis for a sensitive surface analysis technique. Broadband radiation from the bulk of the solid is attributed to the transfer of projectile energy to the electrons in the solid. Continuum emission observed well in front of transition metal targets is believed to arise from excited atom clusters (diatomic, triatomic, etc.) ejected from the solid in the sputtering process. Application of sputtered atom optical radiation for surface and depth profile analysis is demonstrated for the case of submonolayer quantities of chromium on silicon and aluminum implanted in SiO_2.

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INTRODUCTION

The interaction of a confined plasma with the first wall surface constitutes one of the most important problems in the effort to achieve controlled thermonuclear fusion. An important aspect of this problem is that associated with low-energy particle-solid collisions. Experimental investigations of the impact of low energy ions and neutral atoms with solids have found that visible, infrared, and ultraviolet radiation is emitted as a result of the collision[1]. Measurement of the collision induced optical radiation is a powerful tool for studying fundamental processes which result from the interaction of low-energy atomic particles with solids. In addition, optical emission from sputtered particles provides the basis for a sensitive surface analysis technique[2] which may have application as a method for *in situ* detection of impurities on the first wall of a fusion reactor. The purpose of this paper is to describe the kinds of collision induced optical radiation produced in low-energy (20 eV–10 keV) particle-solid collisions and to demonstrate surface and depth profile analysis using this technique.

For the measurements to be described, beams of both ion and neutral atoms have been used. Photons are detected using an f/3.5 monochromator and single photon counting techniques as described elsewhere[2]. Optical measurements have been carried out in the wavelength range 2000Å to 8000Å.

I. Kinds of Collision-Induced Optical Radiation

Both line radiation and broadband continuum radiation are produced in low-energy particle-solid collision. Line radiation arises from excited states of atoms, molecules, and ions that have been sputtered off the surface by the impinging beam and from excited states of reflected beam particles. A significant portion of the sputtered particles leave the surface in excited states

which subsequently decay by photon emission after the excited particle escapes from the solid. Collision induced optical radiation, therefore, provides specific information on the species, quantity, and quantum state of sputtered particles. Line radiation also arises from excited states of reflected beam particles. Measurements of emission line profiles and emission coefficients for H^+ and He^+ (3–30 keV) impacting on metal surfaces have been used to obtain information on the radiationless de-exciation processes which preferentially de-excite low velocity reflected particles[3,4].

At least two kinds of broadband radiation are produced in low-energy particle-solid collisions. Continuum radiation which arises from the bulk of the solid is believed to result from the excitation of electrons in the solid or radiative recombination of electron-hole pairs[1,5]. In some cases continuum radiation is also observed in front of target[6–8]. Experimental results suggest that this radiation arises from excited atom clusters (dimers, trimers, etc.) which have been ejected from the solid in the sputtering process[6,8].

II. Applications of Sputtered Atom Optical Radiation to Surface and Depth Profile Analysis

Optical line radiation arising from sputtered excited atoms gives information on the species of neutral atoms sputtered from the surface and, therefore, provides information on the elemental identity of surface constituents including surface contaminants. This forms the basis for the SCANIIR Surface Analysis Technique[2], a sensitive technique for surface analysis. With this technique, the optical radiation arising from sputtered surface impurities is used for impurity identification, and measurements of the intensity of radiation as a function of bombardment time gives information on depth distribution if the sputtering rate is known. This method requires calibration using samples containing known quantities of impurities on or near the surface.

Figure 1 illustrates the application of this technique for both surface and depth profile analysis and indicates two methods for obtaining detection limits. Figure 1a shows experimental measurements of the intensity of a neutral chromium optical line as a function of bombardment time from silicon samples purposely deposited with chromium as an impurity. Chromium was evaporated to three different levels of concentration on clean silicon wafers, and the surface concentration was measured by 2 MeV Rutherford backscattering. Each sample was then impacted by Ar^+ (8 keV, ~ 4×10^{-5} Amps/cm^2) and the intensity of the CrI-4254Å optical line was measured as a function of bombardment time. Integration of these optical signals should be proportional to the number of chromium atoms removed from the surface and thus to the initial chromium concentration on each sample. The integrated photon signals are in the ratio 1 : 9.2 : 126 which is in reasonable agreement with the concentration ratio as measured by Rutherford backscattering, 1 : 10.6 : 113. The signal/noise ratio from the least contaminated sample is greater than 100 : 1. Therefore, it is not unreasonable to expect that 10^{-3} monolayers of chromium could be detected on a silicon surface, and this level of chromium contamination has recently been determined on chromate treated copper surfaces. Sputtered Cr will be a major impurity in a fusion reactor with a stainless steel wall, and the optical technique is ideally suited to measuring the deposition of sputtered chromium on a collecting substrate at levels greater than 10^{12}/cm^2. These experiments are being extended to the case of Fe and Ni, other major constituents of stainless steel.

From the integrated data of Fig. 1a, we estimate that ~ 5×10^{-4} of all chromium atoms sputtered from this surface give rise to the emission of a CrI-4254Å optical photon. Chromium emits many optical lines and in this case it is possible that up to 1% of all sputtered chromium atoms escape from the surface in excited states. However, the excitation efficiency depends on the sputtered atom and

the nature of the bombarded surface. Both the spectral distribution of radiation and the velocity distribution of radiating atoms can be influenced by non-radiative electron transfer processes[9,10]. This will be particularly important in the case of atoms sputtered from metallic surfaces.

Figure 1b illustrates the application of this technique to depth profile analysis. For this measurement, an SiO_2 film on silicon was implanted by $A\ell^+$(25 keV, $10^{15}/cm^2$). This sample was then impacted by Ar^+ (8 keV, ~ 3×10^{-6} Amps/cm^2) and the intensity of prominent Aℓ and Si optical lines were measured as a function of bombardment time. The significant decrease in the intensity of the Si optical line occurs when the sputtering front reachers the SiO_2/Si interface region. The decrease in optical intensity is attributed to a non-radiative electron transfer process which preferentially de-excites low velocity Si atoms ejected from a silicon surface[9]. The measured time required to reach the SiO_2/Si interface provides an *in situ* method to determine the sputtering rate (~ 22Å/min) if the film thickness is known. The aluminum depth distribution is determined from the sputtering rate and the measured aluminum optical intensity versus time. The dotted line in Fig. 2b is the Gaussian profile fit to a range of 353Å and a standard deviation of 164Å. The fit is reasonable except in the tail of the distribution where the deviation is probably due to recoil implantation of aluminum by the argon beam. From the peak aluminum concentration (1% atomic) and the measured signal/noiseratio (200 : 1) we estimate a detection limit of ~ 5×10^{-3} for aluminum in an SiO_2 matrix.

Data presented in Figs. 1a and 1b demonstrate the application of the optical technique to surface and depth profile analysis. This may have important applications as a probe to determine impurities on the wall of a fusion reactor, or to determine the transport of sputtered material around the perimeter by the use of collecting substrates. In addition, a significant fraction of sputtered

atoms leave the surface in excited states. Ejection of neutral atoms in excited states may influence the radial impurity atom balance in the plasma because sputtered neutral atoms in excited states are more easily ionized on re-entering the plasma than are ground state neutral.

III. Continuum Radiation Produced in Particle-Solid Collisions

Broadband radiation from the bulk of the solid arises from the excitation of electrons in the solid or from radiative recombination of electron-hole pairs created as a result of the loss of projectile energy to the electrons of the solid[1,5]. Broadband radiation of this type is commonly observed when H or He impact on insulating targets (MgF_2, CaF_2, NaI, SiO_2). Fig. 2a shows the spectral distribution of radiation produced by the impact of He°(5 keV) on MgF_2. Measurements of the spatial distribution show that this radiation arises from the bulk of the solid. The spectrum in Fig. 2a has a pronounced peak at 2800Å and subsidiary features at 4100Å and in the range 4800Å to 5800Å. This spectral distribution is also produced by the impact of low energy electrons (~ 1 keV energy) on the crystal. The high energy part of the spectrum in Fig. 2a is similar to that observed in the impact of He°(5 keV) on CaF_2[2]. In the case of CaF_2 this was attributed to radiative recombination of electrons with the self-trapped V_k centers of crystal[2]. For MgF_2, it is likely that the feature at 2800Å also results from radiative recombination of electron-hole pairs of the same type. Features at 4100Å and in the range 4800Å to 5800Å have not been positively identified.

Broadband optical emission which is not localized to the solid has been observed when certain transition metal targets are impacted by low energy ions and neutral atoms[6,8]. One example is shown in Fig. 2b for the case of Ar^{+}(8 keV) on Nb. This spectrum shows numerous atomic lines in the wavelength range 3800Å to 5500Å arising from excited states of sputtered neutral Nb. In addition, there is continuum emission with structure in the wavelength range 2500Å to 3500Å.

Broadband emissions of the type illustrated in Fig. 2b have been observed from transition metal targets whose "d" shells are half filled or less (Mo, Ta, W, Nb, Cr). The more noble metals (Cu, Au, Pt) give rise to little or no continuum emission.

A number of experimental results suggest that these radiative continua arise from excited states of neutral atomic clusters (diatomic, triatomic, or possibly heavier polyatomic species) ejected from the solid in the sputtering process. Detailed measurements[6] of the spatial distribution of both continuum and line radiation have been made in the case of Ar^+ (50 keV) on Molybdenum and are shown in Fig. 3. In Fig. 3, the intensity of Mo atomic line radiation (3798Å) decreases very rapidly as a function of distance in front of the target. In addition two wavelength segments in the radiative continuum from Mo (2960Å, 3450Å) are observed with substantial intensity in front of the target and the continuum intensity decreases less rapidly as a function of distance as compared to the atomic line radiation. These measurements show that a significant portion of the radiative continuum arises well in front of the target and not from the bulk and this strongly suggests that the continuum arises from atom clusters ejected from the solid. The results for continuum radiation in Fig. 3 are consistent with a lifetime of $\sim 2 \times 10^{-5}$ sec. to $\sim 2 \times 10^{-7}$ sec. if we assume that the velocity of the radiating species is in the range 10^4 to 10^6 cm/sec.

The cluster configuration and the electronic transition which gives rise to the radiative continuum from ion bombarded transition metals have not been positively identified. Ion or neutral particle bombardment of the metal target appears to be the only way to excite these continua. Results obtained on biasing the target suggest that the charge of the radiating species is neutral and undetectable by secondary ion mass analysis without preionization. Sputtering of substantial numbers of polyatomic neutral clusters from the first wall and limiter of a fusion device would have important consequences for energy loss to impurities since the cluster would have to be dissociated and the individual

constituents ionized in the plasma.

CONCLUSION

As a result of low-energy particle-solid collisions, the participants in the collision including sputtered particles, reflected particles, and the solid itself can be produced in excited states. Optical radiation arising from these excited states provides insight into the detailed processes of the collision. In addition, radiation from excited sputtered particles uniquely specifies the quantum mechanical state of sputtered neutral particles. This provides the basis for a sensitive method to identify neutral atoms sputtered from surfaces and a method to obtain information on surface composition. This may have application as a method for *in situ* first wall analysis in a fusion reactor or as a means for monitoring the deposition of material sputtered from elsewhere in the reactor by the use of suitable collecting substrates.

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FIGURE CAPTIONS

Fig. 1a Detection of Chromium on Silicon. The intensity of the CrI-4254Å optical line was measured as a function of bombardment time using silicon targets contaminated with chromium.

1b Profile of Aℓ Implanted in SiO_2. Aluminum and silicon optical line intensities were measured as a function of bombardment time.

Fig. 2a Spectral Distribution Produced by the Impact of He° (5 keV) on MgF_2. The broadband continuum is produced in the bulk of the crystal and the weak atomic line at 2852Å arises from sputtered excited Mg atoms.

2b Spectral Distribution Produced by the Impact of Ar^{+} (8keV) on Niobium. Both line radiation and broadband radiation arises in front of the target.

Fig. 3 Spatial Distribution of Line and Continuum Radiation in Front of a Molybdenum Target Impacted by Ar^{+} (50 keV). The target surface is located at Z = 4.2 mm.

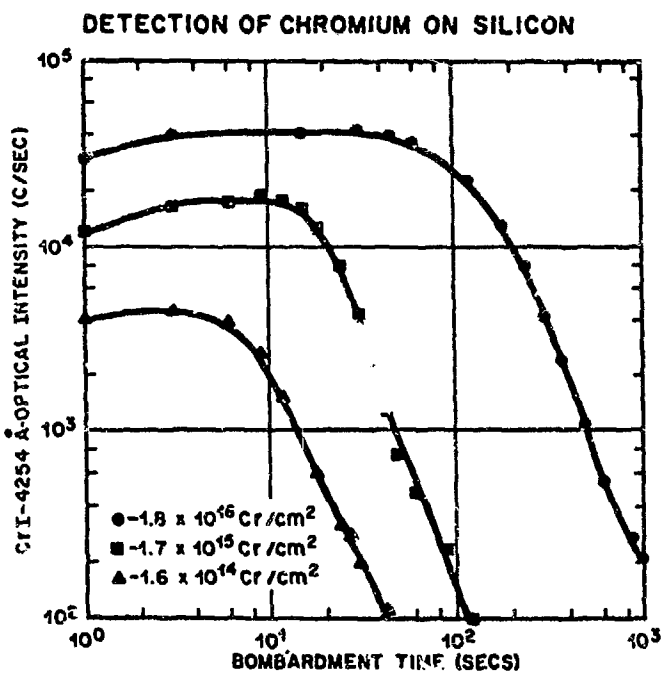
DETECTION OF CHROMIUM ON SILICON
CrI-4254 Å-OPTICAL INTENSITY (C/SEC)
BOMBARDMENT TIME (SECS)
●-1.8 x 10^16 Cr/cm^2
■-1.7 x 10^15 Cr/cm^2
▲-1.6 x 10^14 Cr/cm^2

Fig. 1a

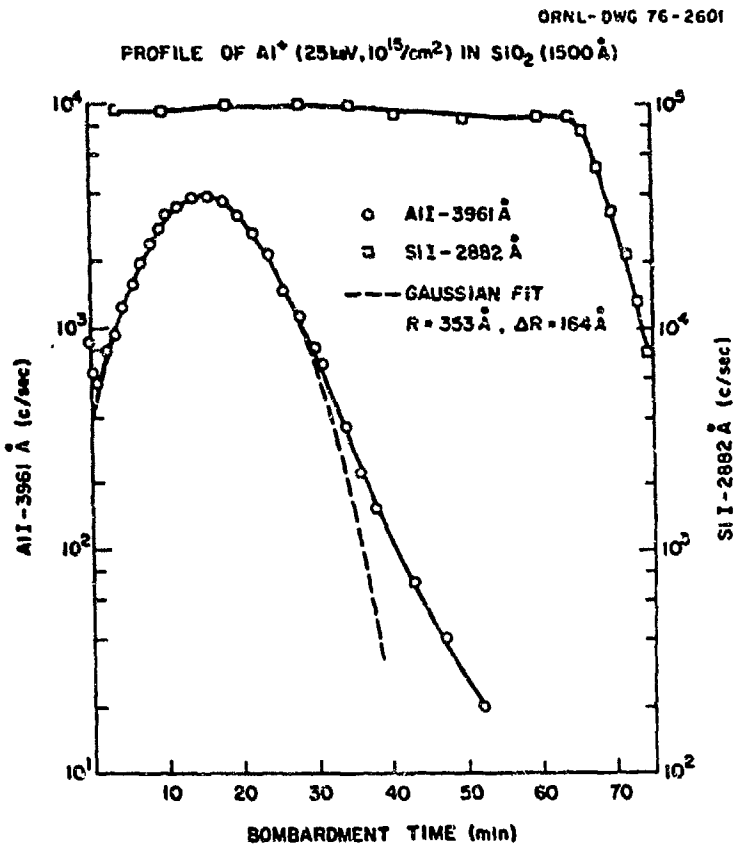
ORNL-DWG 76-2601
PROFILE OF Al+ (25keV, 10^15/cm^2) IN SiO2 (1500 Å)
AlI-3961 Å (c/sec)
SiI-2882 Å (c/sec)
AlI-3961 Å
SiI-2882 Å
GAUSSIAN FIT
R = 353 Å, ΔR = 164 Å
BOMBARDMENT TIME (min)

Fig. 1b

ORNL-DWG 76-2602

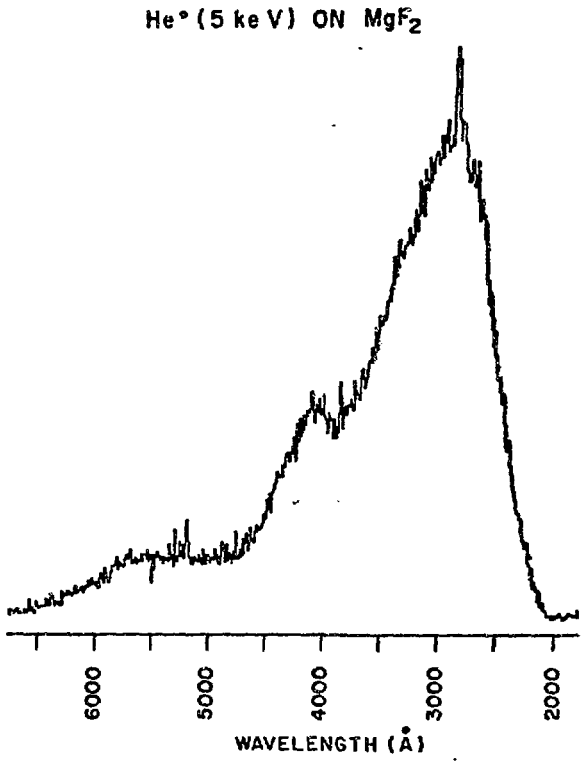

Fig. 2a

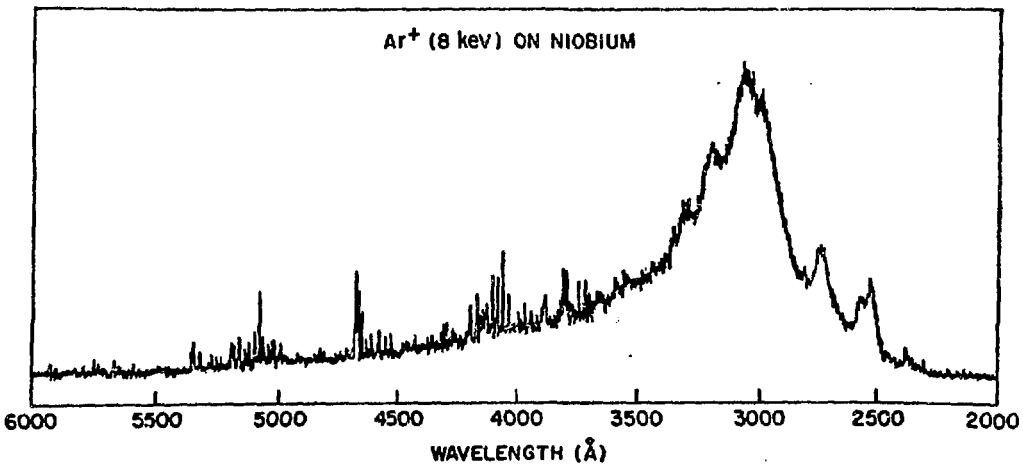

Fig. 2b

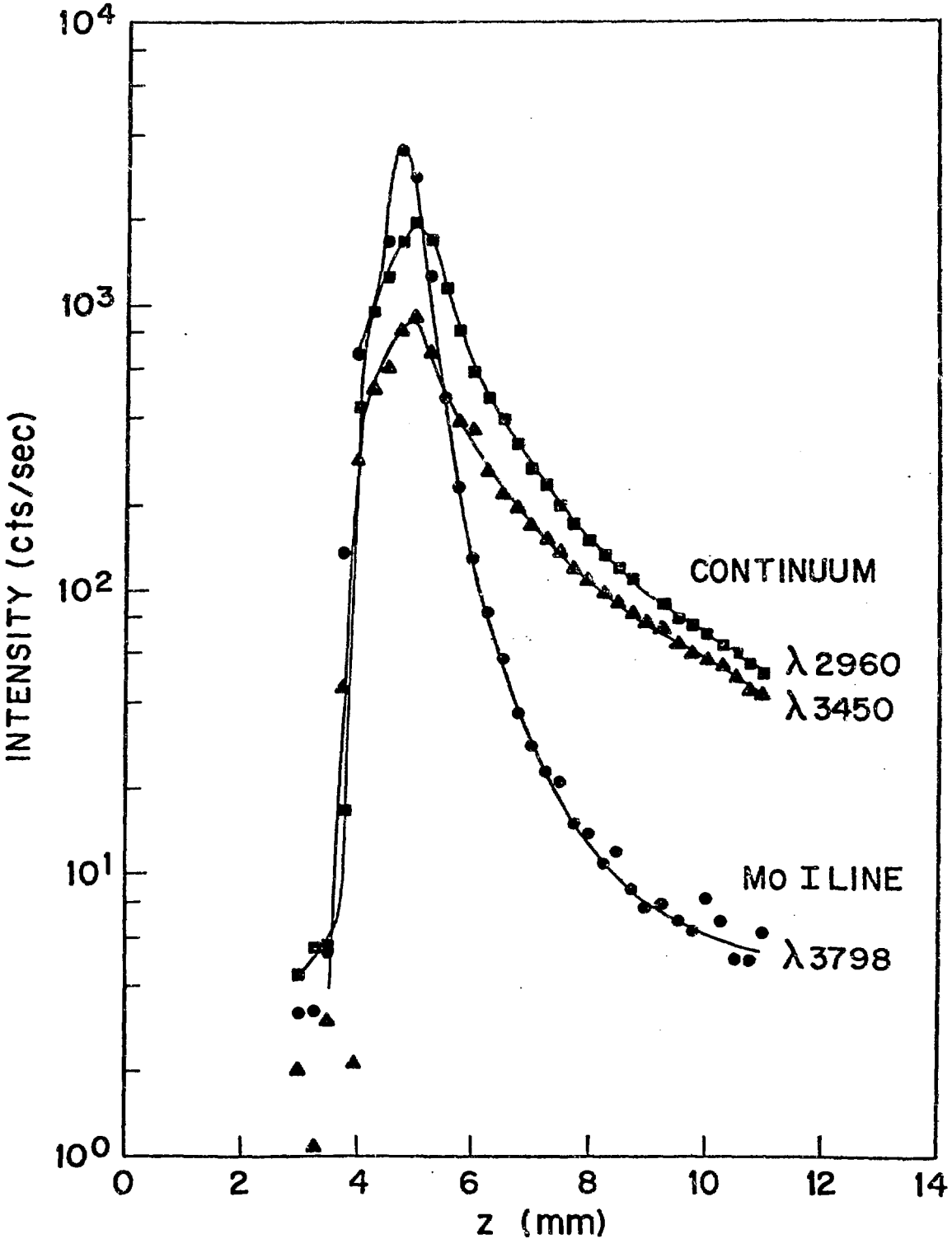
INTENSITY (cts/sec)
10^4
10^3
10^2
10^1
10^0
0
2
4
6
8
10
12
14
z (mm)
CONTINUUM
λ2960
λ3450
MO I LINE
λ3798

Fig. 3