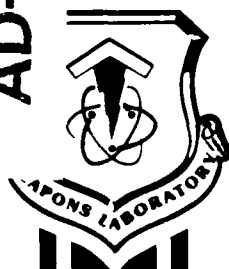


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**PROOF OF PRINCIPLE STUDY OF
THICKNESS MEASUREMENTS USING
CHARACTERISTIC X-RAY LINE
RATIO TECHNIQUES**

Kerry W. Habiger
Charles Stein

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Final Report

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**Weapons Laboratory
Air Force Systems Command
Kirtland Air Force Base, NM 87117-6008**

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FOR THE COMMANDER



STEVEN S. MCCREEDY
Captain, USAF
Chief, Neutral Particle Beam Branch



THOMAS J. SETTECERRI
Lieutenant Colonel, USAF
Chief, Lethality Assessment Division

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1.0 INTRODUCTION

The measurement of the thickness of thin film coatings is important for the research, development and manufacturing of electronic, magnetic, optical and other high-tech materials. Several thin film measurement techniques already exist and are widely used in industry. These techniques include, but are not limited to, the measurement of a single characteristic x-ray line intensity [Ref. 1], x-ray diffraction and Rutherford backscattering spectrometry (RBS) [Refs. 2 and 3].

Years of research and development by the material science community have yielded a wealth of information regarding the use of characteristic x rays for chemical analysis in thin film studies. Scanning electron microscopes (SEM) and transmission electron microscopes (TEM) with energy dispersive x-ray detectors are commonly used in thin film research and manufacturing. Therefore, any technique which can use these existing research tools and improve upon thin film analysis could have an important impact on industry and research.

X-ray techniques which use the intensity of one particular x-ray line to gauge the quantity of a material are not new. Several variations of this technique are already in existence and widely used in industry. One of these techniques uses a control sample substrate bombarded with a fixed fluence of electrons for a fixed amount of time, while an x-ray detector, usually a lithium drifted Silicon (SiLi) crystal, measures the amount of $K\alpha$ x rays generated. Then, the substrate which is coated with a thin film is irradiated at presumably the same electron fluence and energy for the same amount of time in exactly the same geometry, again while a SiLi detector records the amount of $K\alpha$ x rays generated. The reduction in the intensity of the total amount of $K\alpha$ x rays measured from the thin film sample is directly related to the thin film thickness through attenuation. However, problems exist with this technique. The electron beam energy and current can vary between the control sample and thin film sample, slight changes in the detector geometry can be made inadvertently during sample exchange and, because the beam energy is reduced by a factor of dE/dx through the overlay, yield corrections must be made.

Another technique involves using ratios of characteristic x-ray lines to determine the thickness of a thin film overlay. In 1975, various concepts for using ratios of characteristic x-ray lines to measure thicknesses were reported [Ref. 1]. Three methods were offered:

- (a) the ratio between the characteristic x-ray lines of the substrate, such as $K\beta/K\alpha$ or $L\alpha/L\beta$;
- (b) the ratio between the characteristic x-ray lines of the coating; or
- (c) the ratio between the characteristic radiation of the substrate and the characteristic radiation of the coating.

Another ratio of characteristic x-ray lines, the $L/K\alpha$ x-ray line ratio of the substrate was not evaluated in Reference 1. The substrate $L/K\alpha$ x-ray line ratio (where L refers to all of the L series x rays, which are normally indistinguishable from each other) to overlay $K\alpha$ x-ray line ratio could be orders of magnitude more sensitive to thin film thicknesses than the $K\beta/K\alpha$ x-ray line ratio. This is because the L and $K\alpha$ x-ray lines differ in energy by approximately a factor of 10 more than the $K\beta$ to $K\alpha$ x-ray lines of a given substrate. This large energy difference produces a large ratio change when both x-ray lines are attenuated by the overlay. The substrate to overlay x-ray line ratio takes advantage of the added thickness of the overlay to: (1) increase the number of x rays produced in the overlay; and (2) decrease the number of x rays escaping from the substrate, thus changing their ratio.

2.0 THEORY

2.1 INTRODUCTION

When electrons bombard a target, characteristic X rays are produced. The production of X-rays in the target depend upon a number of factors which will be discussed later. As these X rays or photons pass through a material, some are absorbed. This absorption process is responsible for attenuating the original amount of x rays entering the material to a reduced amount of X-rays exiting the material on the other side. As might be expected, the amount absorbed is dependent upon three factors: the energy of the X rays or photons, the element(s) they are passing through, and the density of those elements. Therefore, X ray production and attenuation are the two fundamental concepts behind characteristic x-ray line ratio techniques.

The basic theory that characteristic x-ray line ratios can be used to measure the thickness of a thin film overlay can be best understood by first examining the physics behind x-ray production, attenuation, and some of the factors that may affect them. Discussion of the substrate $K\beta/K\alpha$ ratio technique provides additional background for understanding x-ray line ratios. The first ratio technique investigated theoretically and experimentally uses one X ray from the substrate and one X-ray from the overlay. This ratio changes as X-ray production in the overlay increases and a decreased amount of substrate X rays escapes through the overlay. The second ratio investigated in this study, the substrate $L/K\alpha$ ratio, is similar to the substrate $K\beta/K\alpha$ ratio because it relies solely upon the attenuation of the X-ray lines through the overlay to change its ratio. Theoretical calculations for both ratio techniques studied are given for sample targets used in the experiment.

2.2 PRODUCTION OF CHARACTERISTIC X-RAY LINES

When a target element, Z_2 , is bombarded with photons or particles, Z_1 , individual atoms of the element Z_2 may be ionized. Of course, the probability of ionizing an atom by ejecting an electron from one of its inner orbital shells depends upon the ionization cross section, σ_{KI} or σ_{LI} , for the target atoms, which is a function of the projectile's energy, E_1 , and the binding energy of that atom's particular electron shell. Clearly, the ionization cross section varies for each target element. So, a projectile slowing down

in a target with a rate of energy change per unit change of distance, dE/dx , will have a different ionization cross section throughout the target. This ionization cross section also varies with target element because of the difference in electronic orbital structures, binding energies, and atomic masses.

Once a target atom is ionized by losing an inner shell electron it is in an unstable condition because of the void in one of its inner orbital shells. Thus, the atom attempts to regain its stability by reverting to its original electronic configuration. To do this, an electron from one of the target atom's outer shells may collapse into the vacancy produced in the atom's inner shell by the ionization. When this happens, the collapsing electron must release its excess energy in the form of an X-ray or Auger electron. The characteristic X-ray line and quantity of that characteristic X-ray line released for a given amount of ionizations is given by the fluorescence yield, ω_K , and is a function of the target material and the parameter α , which allows for the dependence of ω_K upon the state of the target initially after the ionizing collision [Ref. 2].

The X-ray production cross sections (σ_{KX} , σ_{LX} , and σ_{MX}) are functions of the ionization cross sections (σ_{KI} , σ_{LI} , and σ_{MI}) and the X-ray fluorescence yields (ω_K , ω_L , and ω_M). The ionization cross section describes the ability of the projectile to eject an electron from one of the atom's inner orbital shells: K, L, or M. The fluorescence yield, which is considered to be independent of the ionization cross section, gives the production probability of a specific X ray, K, L, or M. Consider copper irradiated with 5 keV electrons. The projectiles have enough energy to eject electrons from the copper's L shell, thus ionizing the atom and producing L X-rays, but no K X-rays are produced because the K shell electrons are bound tightly enough so that they are not ejected by the 5 keV projectiles. On the other hand, if copper is irradiated with 30 keV electrons, the copper's K shell electrons are preferentially ejected as compared to those in the copper's L shell, again ionizing the atom, but producing more K X rays than L X rays. However, because the electron projectiles lose energy from collisions in the copper by a function, dE/dx , the ionization cross section and the fluorescence yield of both the K and L shells constantly change with penetration depth.

A relationship for the x-ray production cross section from Reference 2, is shown in Eq. 1. This equation illustrates the complexity of X-ray production by particle bombardment:

$$\sigma_{KX}(Z_1, Z_2, E_1, \alpha) = \omega_K(Z_2, \alpha) \sigma_{KI}(Z_1, Z_2, E_1) \quad (1)$$

Rather than calculating the X-ray production cross sections using energy transport and ionization computer codes, direct experimental measurements of the X-ray line production of substrates bombarded with electrons of various energies were made. These are presented in paragraph 2.4.3.

This description is somewhat oversimplified in that the major orbital shell levels are split into a number of sublevels, i.e., $L_I, L_{II}, \dots, M_I, M_{III}, \dots$, etc [Ref 3]. These additional levels do not change the basic properties, but rather provide an additional identification for each X-ray line. For example, if there is an electron transition from the L_{II} sublevel to fill a void left in the K shell, its excess energy would be given off in the form of a $K\alpha$ X-ray line. However, if there is an electron transition from the L_{III} sublevel to fill the same void left in the K shell by ionization, its excess energy would be given off in the form of a $K\beta$ X-ray line. Likewise, there are several L and M X-ray lines which may exist for each element.

Whether an X ray created by removing an electron from the K shell will be a $K\alpha$ or $K\beta$ X ray is given by the transition probability, which is the probability of a certain sublevel transition happening to fill the void in the K shell. These probabilities, known from quantum mechanics behavior, are important in the substrate $K\beta/K\alpha$ X-ray line ratio scheme, but have little meaning in the other ratio techniques. Reference 4 gives the values of the transition probabilities for each element as ratios in orbital shells K, L, and M. These probabilities are only applicable after ionization and do not take into account self-absorption, an issue to be covered in the next section. It should also be pointed out that transition probability ratios do not exist between different shells because of the production cross section differences.

2.3 X-RAY LINE ATTENUATION THROUGH A THIN FILM

Assuming that characteristic X-rays are produced in an elemental substrate with a thin film coating, they will be absorbed or attenuated as they try to escape through the thin film coating. There are three main mechanisms responsible for the absorption and attenuation of photons in a material: the photoelectric effect, Compton scattering, and pair production [Ref. 5]. Other minor effects exist by which X-ray photons interact with atomic nuclei, but they are negligible. For the attenuation of characteristic X rays (photons of energy < 100 keV) pair production is also a negligible effect and will not be discussed. However, the other two mechanisms are important for understanding the attenuation of X rays and warrant a brief discussion.

In the photoelectric effect, an incident photon collides with a bound electron. The photon's energy ($h\nu$) is absorbed into (or transferred to) the electron during the collision, which is ejected from the atom with a kinetic energy $T = h\nu - I$, where I is the ionization potential of the electron. For all of the photons (X rays) of interest in this study (< 30 keV), the photoelectric effect is the dominant mechanism for attenuation. The cross section for the photoelectric effect decreases rapidly with increasing photon energy, being proportional to $Z^4/(h\nu)^3$ [Refs. 5 and 6].

In Compton scattering, the incident photon is scattered by an atomic electron. The electron is ejected from the atom and the photon scatters off at an angle to its original direction with a reduction in energy. This effect only contributes to the absorption of higher energy X rays > 50 keV. Thus, it is a relatively small effect in the energy regime of 0.5 to 30 keV (Refs. 5 and 6).

All of the mechanisms mentioned play a role in scattering or absorbing a fraction of the X-ray photons passing through a thin film. However, as the photons pass through a thickness dx in the film, fewer and fewer X-ray photons exist which can interact with the film material. The fractional loss of photons by scattering or absorption per unit path length is known as the total linear attenuation coefficient (μ) of the film material. Each process has its own linear attenuation coefficient, which is a function of the process' cross section and the film material. Therefore, a total linear attenuation coefficient is given by

$$\sum \mu_i \quad (2)$$

where μ_i is the linear attenuation coefficient for each separate absorption process. A more readily available and simpler value to use for X-ray attenuation calculations through a thin film is the mass attenuation coefficient (μ/ρ), which depends only on the atomic cross section, Avagadro's number, and the atomic weight [Ref. 5]. Mass attenuation coefficients can be found easily for photons of 0.5 keV up to 1 MeV passing through every possible element. An example plot of the mass attenuation coefficients of aluminum, taken from Reference 7, is shown in Figure 1. It is a plot of the total mass attenuation coefficient, μ/ρ , of aluminum versus photon energy. It also shows the three significant components; the photoelectric effect, Compton scattering, and pair production, that contribute to the total mass attenuation coefficient. The photoelectric effect curve is essentially equal to the total attenuation curve for photon energies $\approx < 10$ keV.

The intensity of photons escaping through a thin film, I , is related to the incident photon intensity, I_0 , the mass attenuation coefficient, μ/ρ , the density of the film, ρ , and the thickness of the thin film, x , by the following equation:

$$\frac{I}{I_0} = e^{-(\mu/\rho)\rho x} \quad (3)$$

which gives the fractional photon beam intensity after attenuation through a thin film. Equation 3 reveals that the attenuation of photons through a film depends exponentially on the product of the mass attenuation coefficient, thickness, and density of the film material. Since the mass attenuation coefficient has a $1/(h\nu)^3$ dependence, the attenuation of photons through a material is extremely sensitive to the energy of the photon. This sensitivity is an important element in changing the ratios of X-ray lines and will be covered in greater detail in paragraph 2.4.

Attenuation of X rays is also an important consideration in the substrate material itself. The self-absorption of an element's X rays leads to the concept of escape depth. As characteristic X rays are generated deep within the substrate and begin to journey out, they are absorbed by the substrate material in which they were produced. Obviously, the deeper the X rays are

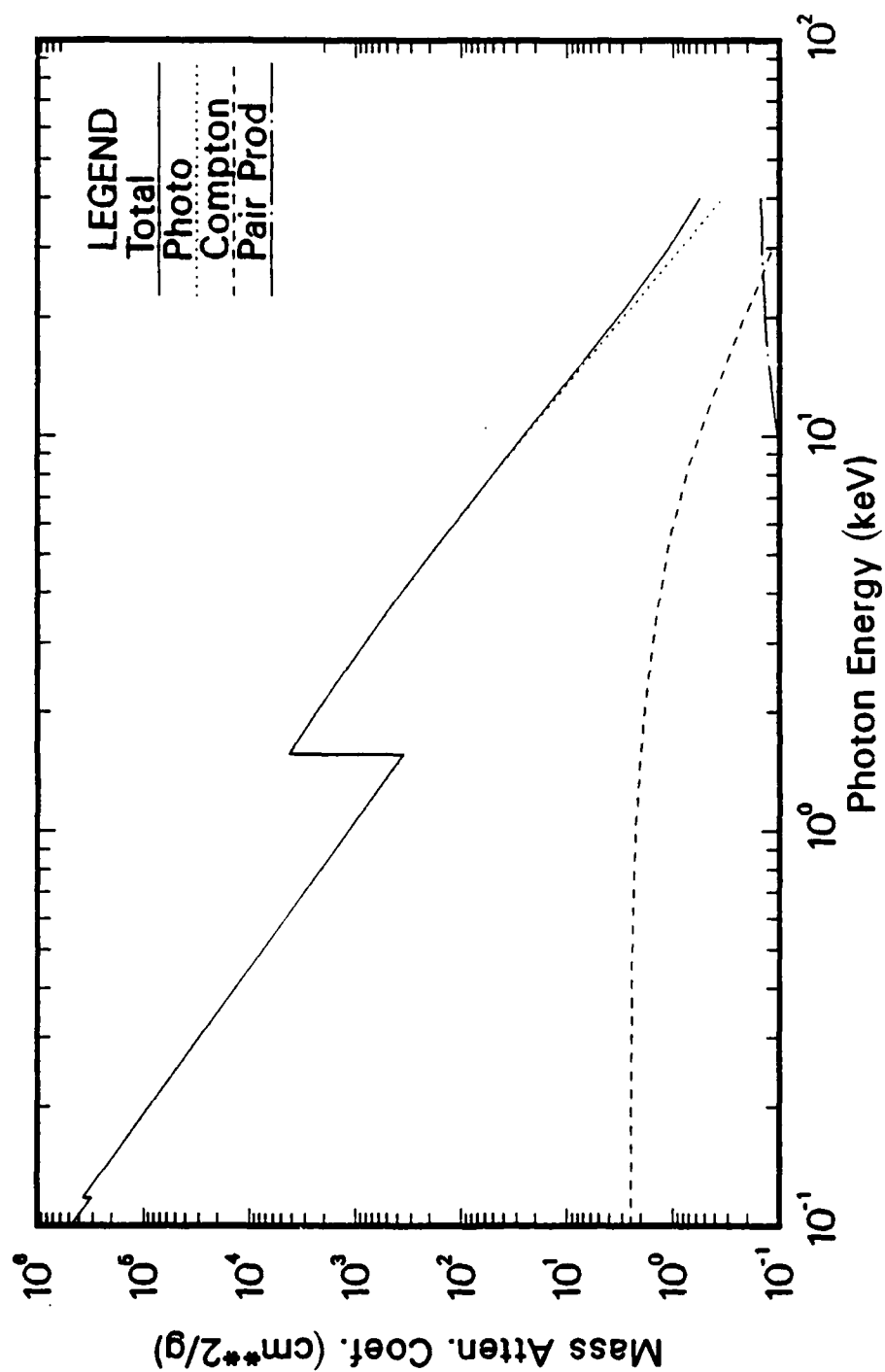


Figure 1. Mass attenuation coefficients for the photoelectric, Compton, pair production, and total effects on a photon passing through aluminum (from Ref. 7).

generated within the target, the better the chances are that they will be absorbed before escaping. The depth at which the amount of X rays generated will be attenuated to a factor of $1/e$ before escaping is the escape depth.

2.4 CHARACTERISTIC X-RAY LINE RATIO TECHNIQUES

The X-ray techniques which use the intensity of one particular X-ray line to gauge the quantity of a material are not new. Several variations of this technique are already in existence and widely used in industry. One of these techniques uses a control sample substrate bombarded with a fixed fluence of electrons for a fixed amount of time, while an X-ray detector, usually a lithium drifted Silicon (SiLi) crystal, measures the amount of $K\alpha$ X-rays generated. Then, the thin film sample is irradiated at presumably the same electron fluence and energy for the same amount of time in exactly the same geometry, again while a SiLi detector records the amount of $K\alpha$ X rays generated. The reduced amount of $K\alpha$ X-rays returned from the irradiated thin film sample is a measure of the X rays attenuated and indicates the sample thickness. However, problems exist with this technique. The electron beam energy and current can vary between the control sample and the thin film sample, slight changes in the detector geometry can be made inadvertently during sample exchange, and, because the beam energy is reduced by a factor of dE/dx through the overlay, corrections must be made. With some care these problems can be controlled and corrected.

In contrast, the X-ray line techniques presented in this report are mainly predicated on ratio methods and do not require rigid control samples or beam monitoring. They use the ratio between two different characteristic X-ray lines from the target. The X-ray lines can both be from the substrate, both be from the overlay, or one can be from the substrate and one from the overlay. These techniques, which use the ratio of two different X-ray lines, may be more sensitive, more accurate, and less vulnerable to errors, but are also more difficult to quantify. While this type of technique may hold the most promise for industry, it also is the one that requires the most research.

2.4.1 The $K\beta/K\alpha$ Ratio

One of the ratio techniques that uses two characteristic X-ray lines from the substrate, is the $K\beta/K\alpha$ ratio. In the $K\beta/K\alpha$ ratio technique, an electron beam

is used to excite the $K\beta$ and $K\alpha$ characteristic X rays from within the substrate material. Because both characteristic X-ray lines are produced from a K shell ionization, the number of $K\beta$ to $K\alpha$ X rays produced will be constant, relative to each other. This ratio holds true as long as the ionizations are random throughout the sample and not part of a large ionization track. The constant $K\beta/K\alpha$ ratio is determined by the K shell transition probability and is different for each material. Since the initial $K\beta/K\alpha$ ratio is invariant to any production mechanisms in the substrate, it can only be changed by the difference caused by attenuation through a thin film.

Since both X rays, $K\beta$ and $K\alpha$, must traverse the same thickness and density of material in a thin film before being detected, they are attenuated by the same material, composition and thickness. But since these two X-ray lines differ in energy, they will be attenuated differently by the thin film, thus changing the initial ratio, R_0 . The new ratio can be directly attributed to the thin film's thickness.

From Eq. 3

$$\frac{I}{I_0}(K\beta) = e^{-(\mu/\rho)_{K\beta} \rho x} \quad (4)$$

and

$$\frac{I}{I_0}(K\alpha) = e^{-(\mu/\rho)_{K\alpha} \rho x} \quad (5)$$

where I/I_0 is the fractional photon intensity after attenuation through the film, $(\mu/\rho)_{K\beta}$ and $(\mu/\rho)_{K\alpha}$ are the mass attenuation coefficients for the $K\beta$ and $K\alpha$ x-ray lines respectively, ρ is the density of the film, and x is the thickness of the overlay film. So the ratio, R , of the $K\beta/K\alpha$ X-ray lines after attenuation is given by

$$R\left(\frac{K\beta}{K\alpha}\right) = \frac{\frac{I}{I_0}(K\beta)}{\frac{I}{I_0}(K\alpha)} = R_0 e^{-\rho x \left[(\mu/\rho)_{K\beta} - (\mu/\rho)_{K\alpha} \right]} \quad (6)$$

which is the ratio of the fractional intensities, I/I_0 , of the $K\beta$ and $K\alpha$ characteristic X-ray lines multiplied by the initial ratio, R_0 . Solving Eq. 6 for the thickness of the thin film yields

$$\rho x = \frac{-\ln(R/R_0)}{\rho[(\mu/\rho)_{K\beta} - (\mu/\rho)_{K\alpha}]} \quad (7)$$

Thus, given the measured final ratio, R , after attenuation, the initial known ratio, (R_0) , the thin film density and the attenuation coefficients of the $K\beta$ and $K\alpha$ lines, the thickness of the thin film can be determined.

However, because of the close proximity in energy of the $K\beta$ and $K\alpha$ X-ray lines for most elements, very little ratio change occurs through thin films, especially when the film is made of a low Z element. From Eq. 6, it can be seen that the difference in $(\mu/\rho)_{K\beta}$ and $(\mu/\rho)_{K\alpha}$, which are functions of the $K\beta$ and $K\alpha$ X-ray energy respectively, determines the amount the $K\beta/K\alpha$ ratio will change. For example, consider a copper substrate with values of $K\beta = 8.9$ keV, $K\alpha = 8.04$ keV, and $R_0 = 0.1365$, coated with 5000 Å of aluminum with a $\rho = 2.7$ g/cm³ bombarded with electrons. Using the tabulated values of Figure 1, where $(\mu/\rho)_{K\beta} = 37.05$ cm²/g and $(\mu/\rho)_{K\alpha} = 50.09$ cm²/g, Eq. 6 yields an expected measured ratio of $R = 0.1367$, which is only a 0.176 percent change from R_0 . Obviously, measurement of thin films below 10,000 Å with the substrate $K\beta/K\alpha$ ratio technique is questionable at best.

2.4.2 The Substrate To Overlay X-Ray Line Ratio

As the overlay thickness increases, the production of overlay X rays from electron bombardment increases. In addition, the increased overlay thickness attenuates a larger fraction of the substrate's X-ray photons trying to escape through the thin film overlay. Consequently, the situation is unique in that the two characteristic X-ray lines change in the opposite direction, one increasing and one decreasing, thereby increasing the sensitivity of the ratio change dramatically with small changes in overlay thickness. This effect shown mathematically is

$$R = \frac{D_s}{D_o} \quad (8)$$

where R is the ratio measured at the detector, and D_s and D_o are the number of X rays detected from the substrate and overlay, respectively. The number of X rays generated in the substrate and detected through the thin film overlay is given by

$$D_s = \left[\int_0^1 Y_s e^{-(\mu/\rho)_{ss} \rho_s x_s} dx \right] e^{-(\mu/\rho)_{so} \rho_o x_o} \quad (9)$$

where Y_s is the average X-ray yield per unit length within the substrate, $(\mu/\rho)_{ss}$ is the mass attenuation coefficient of the substrate x-ray line in the substrate material (self-absorption), ρ_s is the density of the substrate material, and x_s is the thickness of the substrate. Likewise, $(\mu/\rho)_{so}$ is the mass attenuation coefficient of the substrate line in the overlay material, ρ_o is the density of the overlay material, and x_o is the thickness of the overlay. The upper integration limit is 1 cm, the thickness of the substrates used in the experiments. The term inside the brackets is the number of substrate X rays escaping. It takes into account the substrate's X ray production by electron bombardment and the attenuation by self-absorption. The term outside of the brackets accounts for the attenuation of the substrate's X-ray lines through the overlay.

Integrating Eq. 9 yields

$$D_s = \left[\frac{Y_s}{(\mu/\rho)_{ss} \rho_s} \right] e^{-(\mu/\rho)_{so} \rho_o x_o} \quad (10)$$

Equation 10 can be reduced again by using the concept of the escape depth, which was defined as the depth at which the amount of X rays generated will be attenuated to a factor of $1/e$ before escaping. The escape depth (X_E) is just

$$X_E = \frac{1}{(\mu/\rho) \rho} \quad (11)$$

Using Eq. 11, Eq. 10 reduces to

$$D_s = [Y_s X_E] e^{-(\mu/\rho)_{so} \rho_o x_o} \quad (12)$$

In a similar fashion the number of X-rays detected from the overlay caused by electron bombardment can also be derived mathematically.

$$D_o = \int_0^{x_o} Y_o e^{-(\mu/\rho)_{oo} \rho_o x'} dx' \quad (13)$$

In this case, the upper limit is the thin film thickness and the number of overlay X rays exiting the surface of the film is given by the integrated yield per unit length multiplied by the self-absorption in the film.

Integrating Eq. 13 yields

$$D_o = \frac{Y_o}{(\mu/\rho)_{oo} \rho_o} \left(1 - e^{-(\mu/\rho)_{oo} \rho_o x_o} \right) \quad (14)$$

As Eq. 14 illustrates, the exponential term of the overlay yield does not go to zero, as in Eq. 10 because x is very small in this case ($< 10^{-4}$ cm) compared to 1 cm in Eq. 10.

Using Eqs. 12 and 14, a relation for the ratio, R , of the substrate X-ray line to the overlay X-ray line can be found.

$$R = \left(\frac{Y_s X_E (\mu/\rho)_{oo} \rho_o}{Y_o} \right) \frac{e^{-(\mu/\rho)_{so} \rho_o x_o}}{\left(1 - e^{-(\mu/\rho)_{oo} \rho_o x_o} \right)} \quad (15)$$

Since the factors in the first term are all assumed to be constants, they can be combined into one constant, K . Therefore, Eq. 15 becomes

$$R = K \frac{e^{-(\mu/\rho)_{so} \rho_o x_o}}{\left(1 - e^{-(\mu/\rho)_{oo} \rho_o x_o} \right)} \quad (16)$$

Using Eq. 16 and assuming a value of 1 for K , the theoretical curves of R versus the overlay thickness, x_o for a copper substrate coated with aluminum and a molybdenum substrate coated with aluminum are shown in Figures 2 and 3, respectively. The constant K , assumed to be 1 for these calculations, is the yield per unit length multiplied by the escape depth of the substrate X-ray

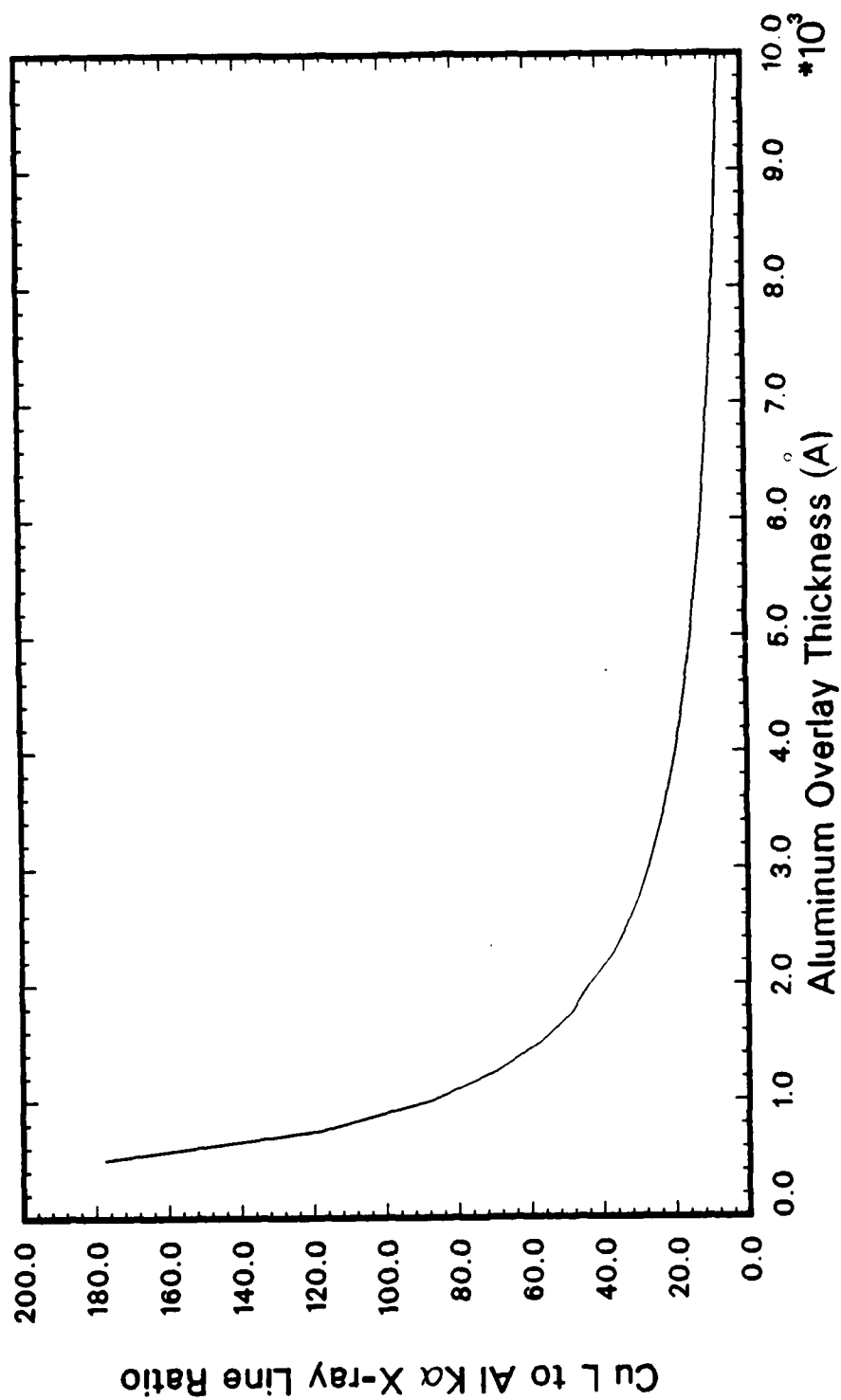


Figure 2. Calculated ratio of the copper L X-ray line to the aluminum K α X-ray line versus the aluminum overlay thickness.

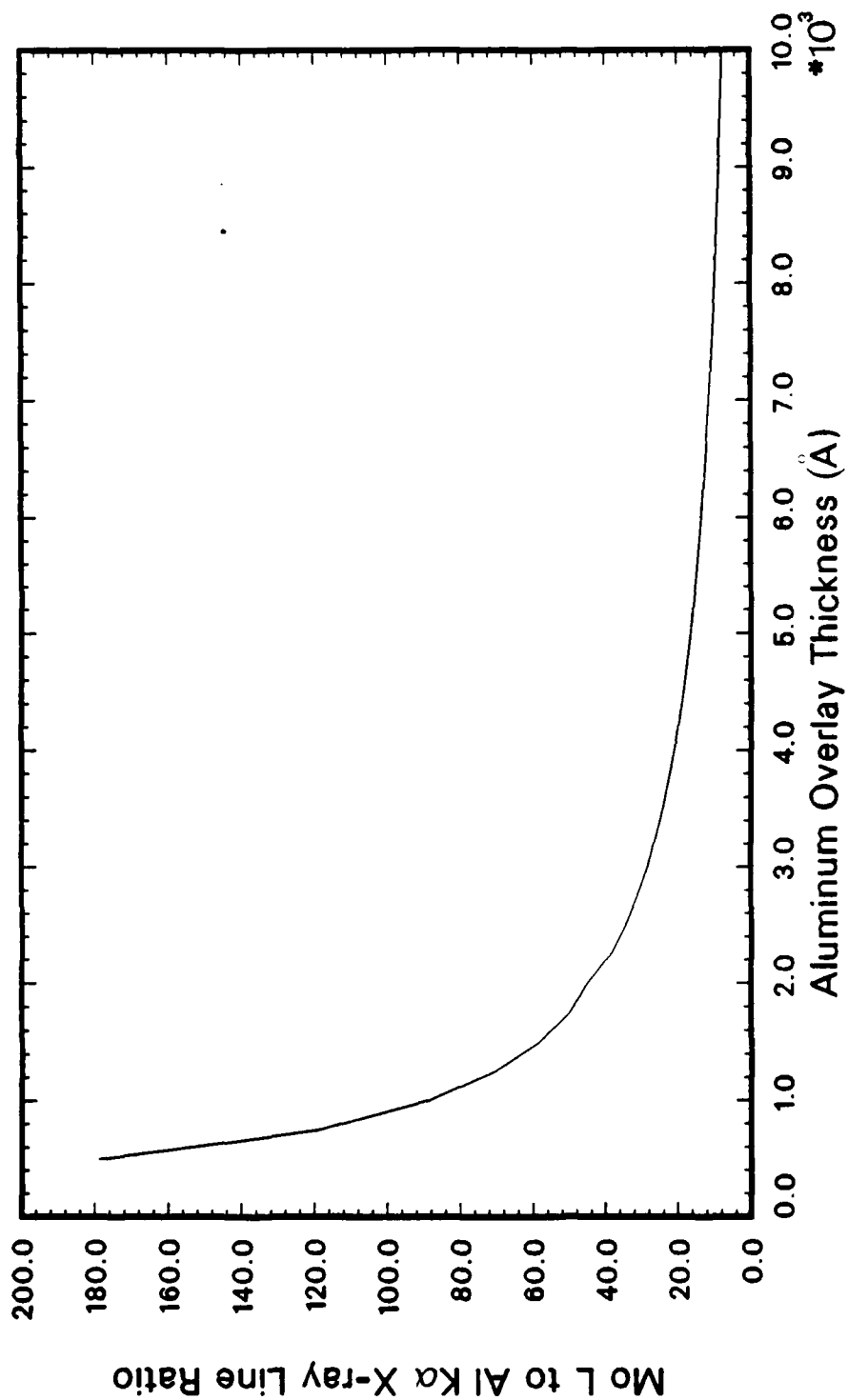


Figure 3. Calculated ratio of the molybdenum L series X-ray line to the aluminum K α X-ray line versus the aluminum overlay thickness.

line divided by the yield per unit length multiplied by the escape depth of the overlay X-ray line. The X-ray yields, Y_s and Y_o , from electron bombardment are a function of the electron energy and target material (Z). However, since the X-ray yields from electron bombardment of copper, molybdenum and aluminum are on the order of 1×10^{-4} and $1/(\mu/\rho)\rho$ of the overlay and the substrate (X_E) are within a factor of 2 or 3 of each other, the value of K can be approximated as 1 for a first order analysis.

Examination of Figures 2 and 3 show that the ratio has a $1/x$ dependence. This can be verified mathematically by expanding the denominator of Eq. 16 into a Taylor series. Equation 16 becomes

$$R = K' \frac{e^{-(\mu/\rho)_{so} \rho_o x_o}}{\frac{1}{(\mu/\rho)_{oo} \rho_o} \left[1 - \left(1 - (\mu/\rho)_{so} \rho_o x_o + \frac{(\mu/\rho)^2 \rho^2 x_o^2}{2!} - \dots \right) \right]} \quad (17)$$

where

$$K' = \frac{K}{(\mu/\rho)_{oo} \rho_o}$$

Collecting terms and factoring Eq. 17 yields

$$R = K' \frac{e^{-(\mu/\rho)_{so} \rho_o x_o}}{x_o \left[1 - \frac{(\mu/\rho) \rho x_o}{2!} + \frac{(\mu/\rho)^2 \rho^2 x_o^2}{3!} - \dots \right]} \quad (18)$$

But, when x_o is small ($< 10^{-4}$ cm) Eq. 18 reduces to

$$R = K' \frac{e^{-(\mu/\rho)_{so} \rho_o x_o}}{x_o} \propto \frac{1}{x_o} \quad (19)$$

2.4.3 The Substrate L/K α Ratio

Derivation of the substrate ratio, L/K α , is similar to that for the substrate K β /K α theory. Both ratio techniques work on the same premise of X-ray line attenuation through a thin film. However, the characteristic L X-ray line of the substrate is ≈ 10 times lower in energy than the K α X-ray line. Theoretically, this energy difference will increase the substrate L/K α X-ray line

ratio sensitivity to thin films. This assumption is based solely on the large mass attenuation of the "soft" L characteristic X-ray line as compared to that of the $K\alpha$ characteristic X-ray line yielding a larger ratio change than the $K\beta/K\alpha$ ratio technique.

As in the substrate $K\beta/K\alpha$ ratio technique, an electron beam is used to excite the characteristic X rays in the substrate. However, the factors affecting the production of X rays by electron bombardment are not as straightforward in the L/ $K\alpha$ ratio technique. The cross sections for ejecting an electron out of the L shell and K shell will be different for each electron energy. Thus, the L and K shell X-ray cross sections change as the beam changes energy while traversing the target. Also, because of the large energy difference between the L and $K\alpha$ X-ray lines, their escape depths are drastically different. To correctly quantify all of these factors would be a major project using particle energy transport codes and complicated X-ray production codes. Instead, a simplified, straightforward approach was used here with the following assumptions.

The first assumption was that an initial ratio, R_0 , could be measured from the substrate material at the electron energy to be used for the ratio measurement experiments. To determine whether or not this was a valid assumption, a simple experiment was carried out by measuring the substrate's L/ $K\alpha$ X-ray line ratio at varying electron beam energies. Figure 4 shows the copper L/ $K\alpha$ ratio versus electron accelerating energy. Examination of Figure 4 shows a relatively small change in the initial ratio was observed at higher electron voltages. But, the impact on the initial ratio becomes greater as the electron energy decreased toward 20 and 15 keV because of the large L and K shell ionization cross section changes associated with the low beam energy. A simple calculation showed that an aluminum film of 5000 Å only decreased (dE/dx) the electron energy by 1 keV as it traversed the thin film. Therefore, the electron energy is much less important to the L/ $K\alpha$ ratio than the thin film attenuation effect at high energies.

Theoretically, the thickness, x , can be obtained from Eqs. 4 to 7 by replacing the $K\beta$ X-ray line mass attenuation coefficient with that of the L X-ray line mass attenuation coefficient, yielding

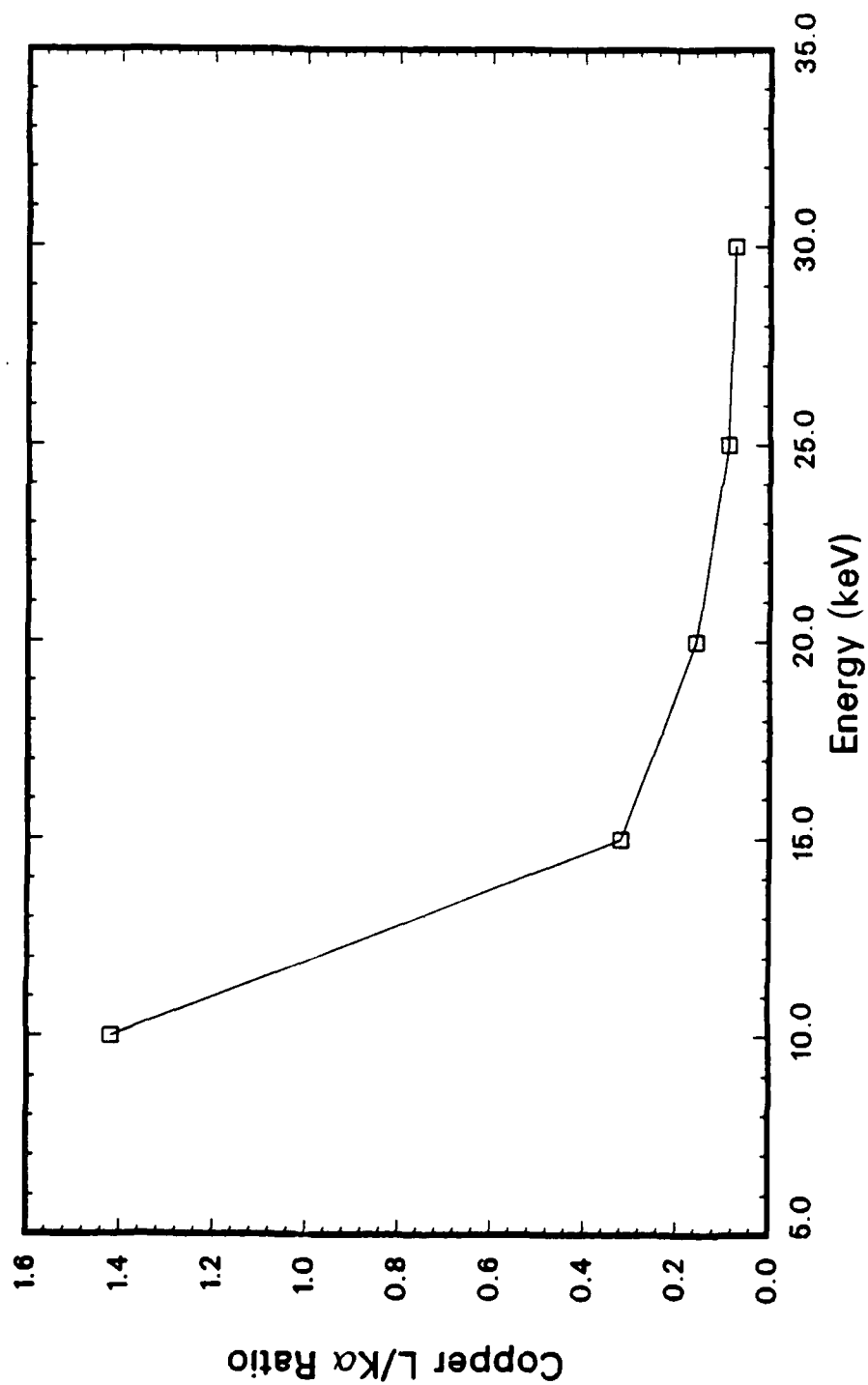


Figure 4. Measured copper L/K α ratio versus energy of electron bombardment.

$$x = \frac{-\ln[R/R_0]}{\rho \left[(\mu/\rho)_L - (\mu/\rho)_{K\alpha} \right]} \quad (20)$$

where R_0 is the calibrated initial ratio of the substrate, R is the final ratio, $(\mu/\rho)_L$ is the mass attenuation coefficient of the L X-ray line through the film, and $(\mu/\rho)_{K\alpha}$ is the mass attenuation coefficient of the $K\alpha$ X-ray line through the film. Figures 5 and 6 show the theoretical percent change in the substrate L/ $K\alpha$ X-ray line ratio versus the aluminum overlay thickness for copper coated with aluminum and for molybdenum coated with aluminum, respectively. As expected, Figures 5 and 6 show that the L/ $K\alpha$ X-ray line ratio decreases exponentially with overlay thickness.

The difference in sensitivity between the L/ $K\alpha$ and $K\beta/K\alpha$ ratio techniques can be shown by using Eq. 6 and the same example as used before to compare the ratio change of a copper substrate coated with an aluminum overlay. The copper $K\alpha$ X-ray line is equal to 8.04 keV with a mass attenuation coefficient through aluminum of $(\mu/\rho)_{K\alpha} = 50.09 \text{ cm}^2/\text{g}$. Also, the aluminum thickness $x = 5000 \text{ \AA}$ and the density of aluminum, $\rho = 2.7 \text{ g/cm}^3$ as before. But, this time using the copper L line of 0.9 keV, its mass attenuation coefficient through aluminum of $(\mu/\rho)_L = 1557 \text{ cm}^2/\text{g}$, and from Figure 4, $R_0 = 0.073$, yields an expected measured ratio, $R = 0.0596$, a change of 18.4 percent. Obviously, this change can be reasonably measured and used to determine the thickness of thin films.

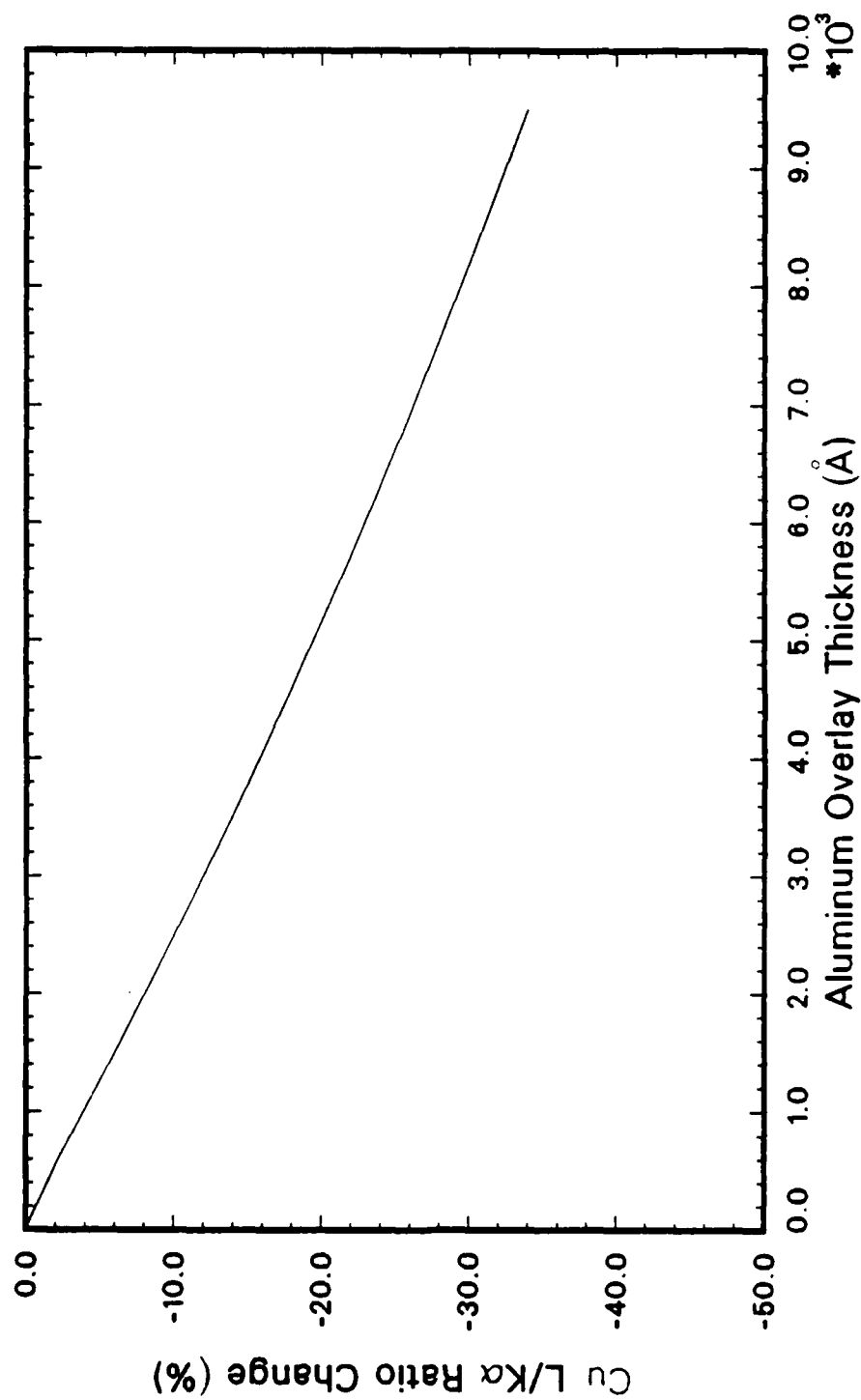


Figure 5. Percent change in transmitted copper L/Kα ratio versus aluminum overlay thickness.

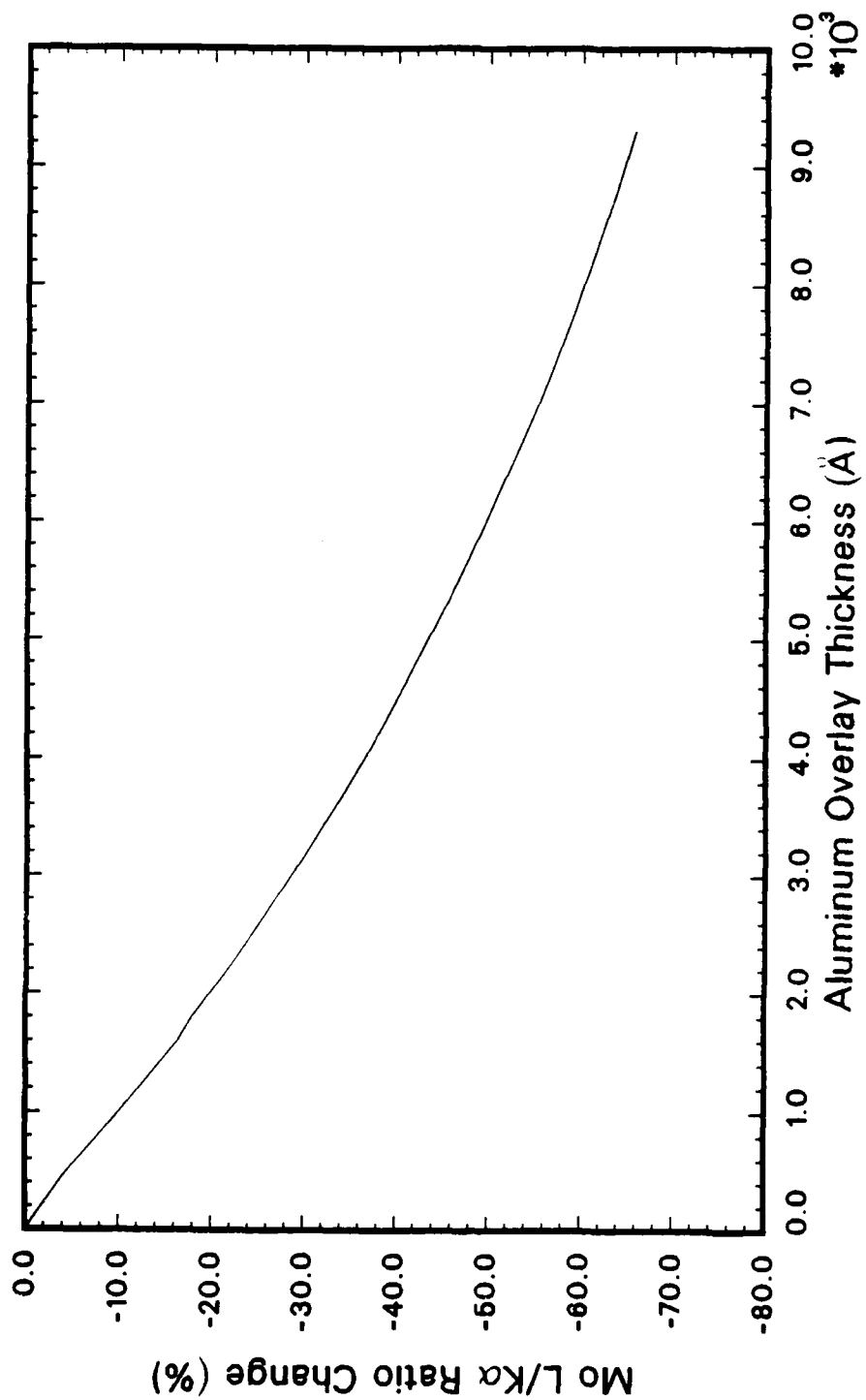


Figure 6. Percent change in transmitted molybdenum L/K α ratio versus aluminum overlay thickness.

3.0 EXPERIMENT

3.1 SAMPLE PREPARATION

To increase the chances of conducting a successful experiment yielding data that may be easily interpreted, the test sample set must be chosen with care. For this experiment the sample set was chosen from materials that are easily coated, can be found in a high degree of purity, and have well-known densities, which typically means that their mass attenuation coefficients are also well known. Thin film overlays that are not uniform will have wide variations in density and thickness. Impurities will also affect the density of a film and its mass attenuation coefficient. Those considerations limited the choices to these high purity metals: copper, aluminum, gold, silver, titanium, and molybdenum.

Copper and molybdenum were chosen as the substrate materials for the experiment. Both emit $K\alpha$, $K\beta$, and L X-ray lines in the energy region easily excited by the SEM and easily measured by the detection system. Aluminum was selected as the overlay coating because it is easy to deposit and low enough in Z to allow the application of thicker films which permit the X-ray line ratio techniques to be tested over a large range of thicknesses, with a lower tolerance in the thin film thickness accuracy and measurement.

Both substrate materials were prepared and coated in the Weapons Laboratory's Metrology Laboratory. The substrates consisted of 99.999 percent pure copper and molybdenum, 1-cm-thick, optically polished disks. Each disk was coated with aluminum in thicknesses varying from 400 to 7000 Å by ion beam techniques. During the aluminum deposition, a crystal oscillator thin film measurement was taken. After the aluminum deposition, each overlay thickness was measured with a tally step. Both thin film measurements were within ± 10 percent of each other, even though the tally step resolution was no better than ± 5 percent.

3.2 DATA COLLECTION

All of the experiments were carried out on an SEM located in the Weapons Laboratory's Material Science Laboratory. This particular SEM is capable of

accelerating electrons up to 30 keV in 5 keV steps. The electrons bombarded the coated sample perpendicular to the sample's surface at a distance of 30 mm from the final lens.

The X-ray spectra were recorded with an energy dispersive, liquid nitrogen cooled, SiLi detector. It was mounted on the SEM at a take off angle of 28 deg from the horizontal, or 118 deg in the backscatter direction and 15 cm from the sample. To maintain this critical angle for each sample, the position of the sample stage was kept constant, as was the SiLi detector's orientation and geometry. This orientation, however, increased the actual path length a photon had to traverse in aluminum before escaping in the direction of the SiLi detector, by a factor of $1/\sin(28 \text{ deg})$. Therefore, a thin film of 300 Å on the substrate actually was treated as a 639 Å thin film in the direction of the detector.

The signal from the SiLi detector was amplified, shaped, and recorded by standard x-ray analysis hardware and software. The software included peak finding routines as well as standard energy calibrations. The SiLi detector used in this experiment is > 80 percent efficient in the energy range of 1.5 to 27 keV with a 0.0075 mm beryllium entrance window. Its peak efficiency is from 4 to 18 keV with a resolution of 125 eV. However, since this experiment measured and compared ratios of characteristic X-ray lines, the entrance window and detector efficiency were not important as long as they were consistently maintained throughout the test.

3.3 DATA ANALYSIS

The recorded X-ray spectra were transferred from the collecting computer to the Weapons Laboratory's VAX-8700 computer for analysis. The data analysis on the Weapons Laboratory's VAX-8700 was done with a FORTRAN computer code called RATIO_ANAL written especially for this project. This code allowed the user to obtain a least squares Gaussian peak on a linear background fit of the characteristic X-ray lines. The inputs allowed the user to choose the number of peaks to fit, number of fitting iterations, beginning and ending energy of the spectrum to be fit, and the absolute and relative fitting tolerances. Another required input to the program was an estimate of each peak's height,

center and width along with the background slope and intercept. These values were used as starting parameters and then varied to obtain the best fit.

The program, `RATIO_ANAL`, called several subroutines. Subroutine `FITIT` estimates a nonlinear function's parameters by a least squares algorithm [Ref. 8]. After obtaining the best fit to the data and subtracting the background, `FITIT` returns the theoretically best fit parameters of the function. The subroutine `FITIT` also required subroutines supplied by the user. Subroutines `GAUSS`, `DGAUSS`, `PEAKS` and `DPEAKS` had to be written and supplied to `FITIT`. The subroutine `GAUSS` is a Gaussian function and `DGAUSS` provides its derivatives. The subroutines `PEAKS` and `DPEAKS` allowed the fitting of multiple Gaussian functions. All of the calculations and experimental data were plotted with a program called `SIMPLOT*`.

The accuracy in the data analysis is one of the most important parts of the experiment because the areas of each peak, used to compute the X-ray line ratios, are determined by the fit parameters. Subroutine `FITIT` is used to obtain the best possible fit and return the parameters of the height and width of each peak. Then the ratios of the areas are computed. Great care was taken in ensuring that the peak fits were accurate and consistent. Examples of the analysis accuracy in fitting raw data are illustrated in Figures 7 through 10.

Figure 7 shows the X-ray spectrum of a copper substrate coated with 2482 Å of aluminum bombarded with 30 keV electrons. Figure 8 shows the Gaussian fit (solid line) compared to the raw data (points) of the copper L and aluminum K α X-ray lines of these data. Figure 8 illustrates the accuracy of the data analysis technique. However the molybdenum samples proved to be more of a challenge. Figure 9 shows the X-ray spectrum of a molybdenum substrate coated with aluminum. Upon close inspection of Figure 9, the molybdenum characteristic L X-ray line actually consists of a series of X rays (L β_1 , L α and L β_2) lying on top of each other. Figure 10 is the same data with the aluminum K α and molybdenum L series X-ray lines fit to Gaussian functions. It shows that the analysis routines used for the experiment are capable of accurately analyzing difficult X-ray spectra.

*Available through the authors.

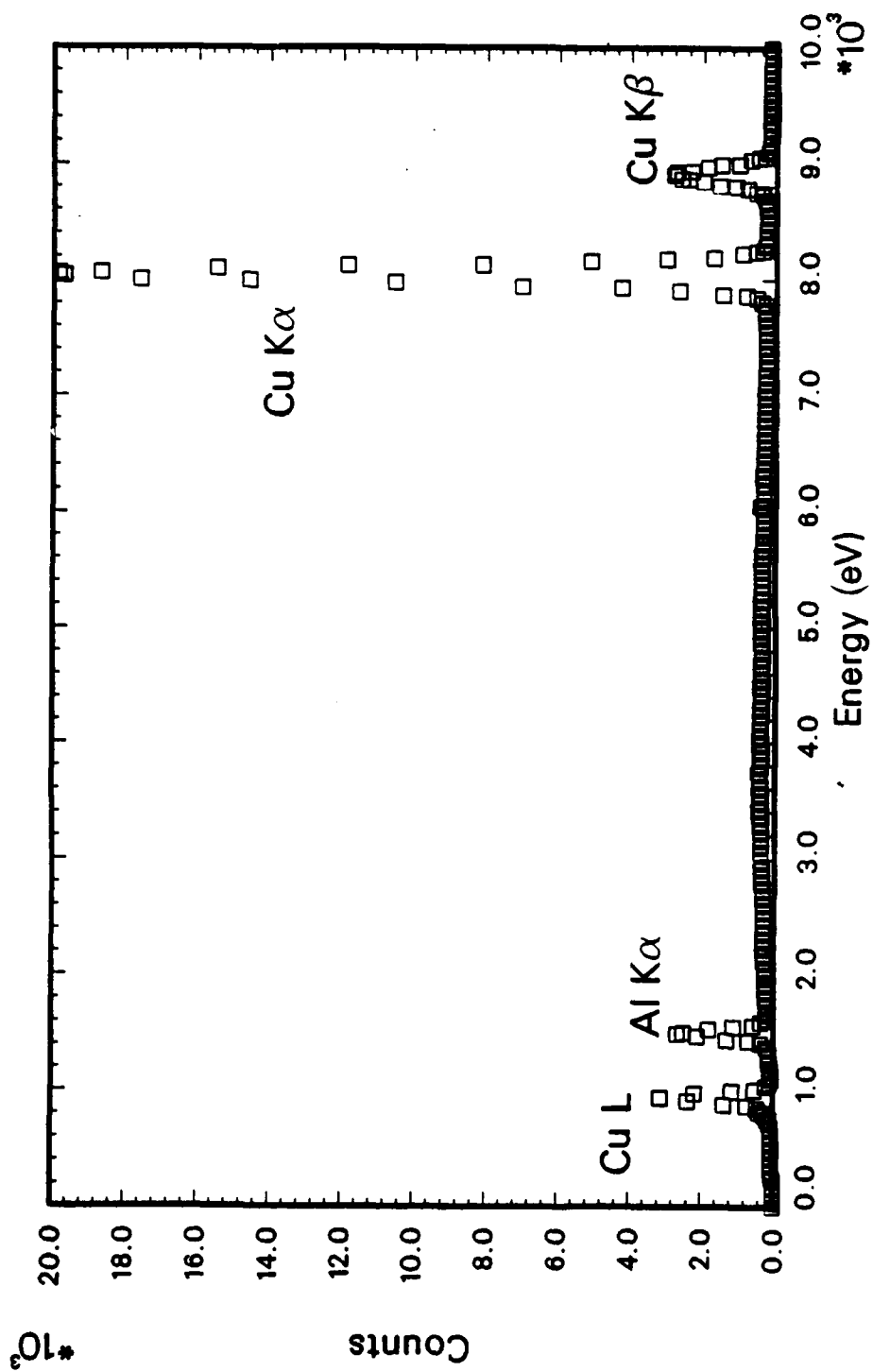


Figure 7. The X-ray spectrum of a copper substrate coated with 2428 Å of aluminum and bombarded with 30 keV electrons.

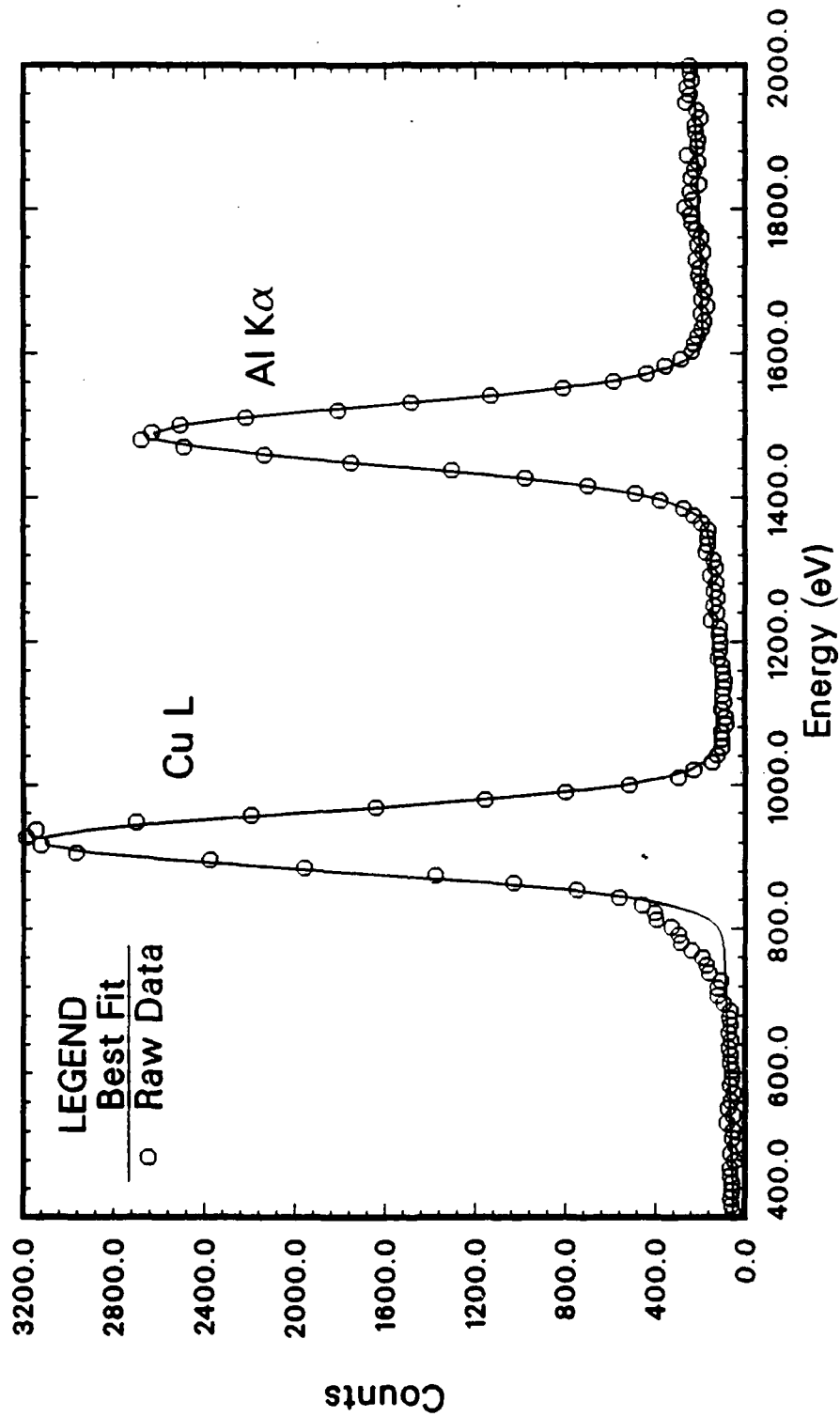


Figure 8. Theoretical Gaussian fit of the copper L and aluminum Ka peaks compared to the raw data.

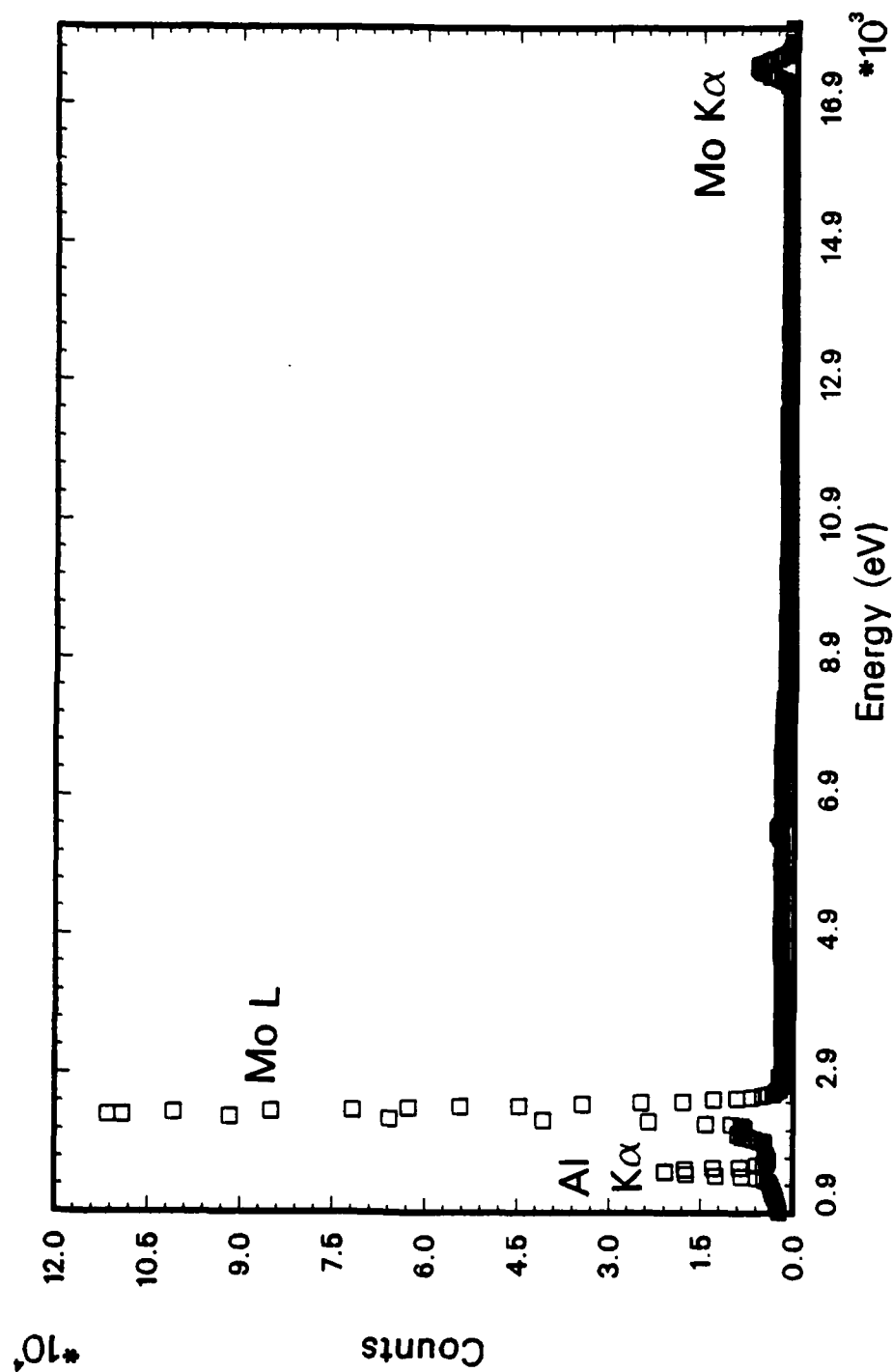


Figure 9. The X-ray spectrum of a molybdenum substrate coated with 2982 Å of aluminum and bombarded with 30 keV electrons.

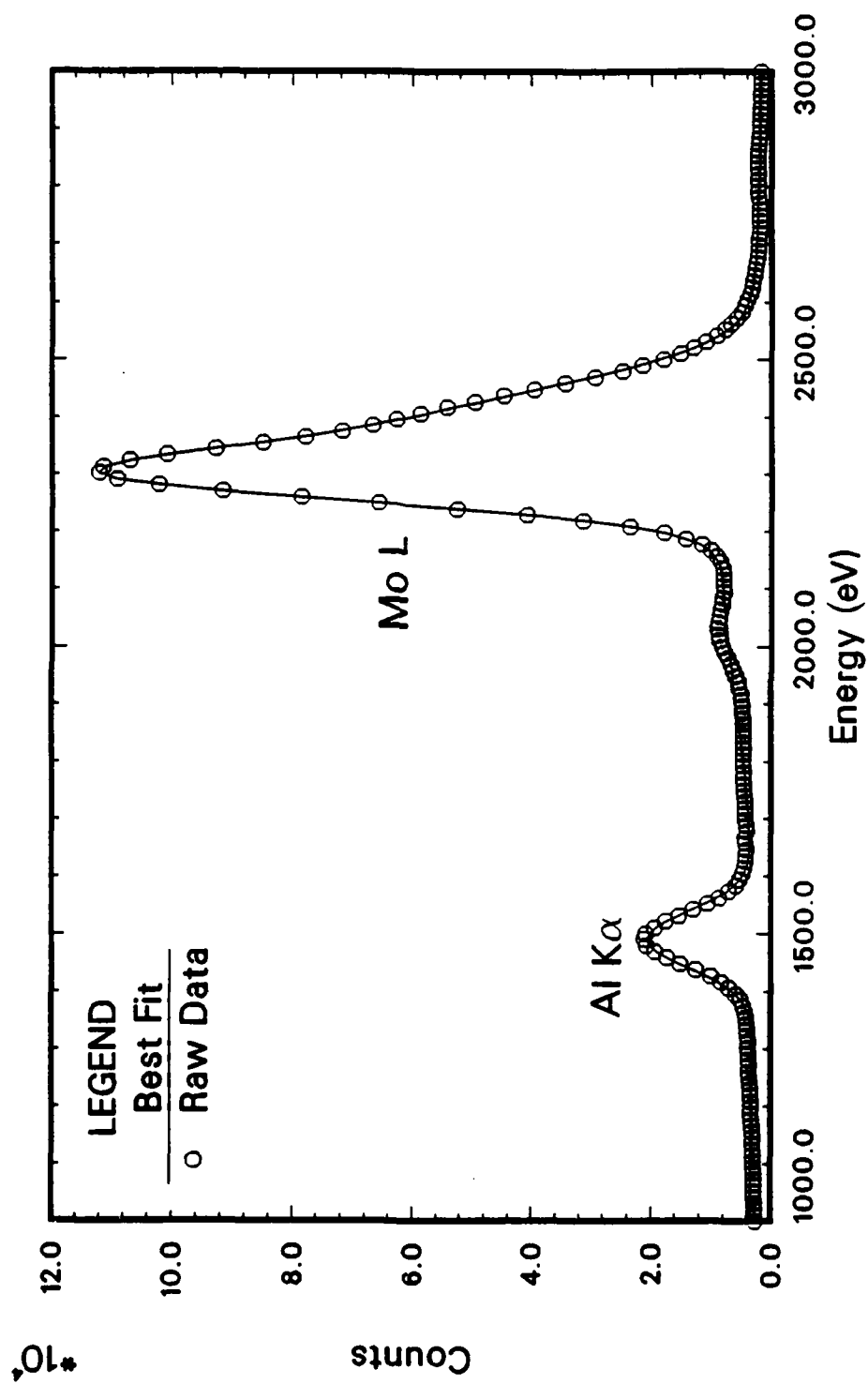


Figure 10. Theoretical Gaussian fit of the aluminum K α and molybdenum L series peaks compared to the raw data.

4.0 EXPERIMENTAL RESULTS

4.1 INTRODUCTION

The characteristic X-ray line ratios were determined from each sample in the following manner. After the substrate was coated with aluminum and the aluminum thickness measured with the tally step, it was irradiated in the SEM at 20, 25 and 30 keV. The SiLi detector recorded the X-ray spectrum for ≈ 30 min. The X-ray spectrum was transferred to the VAX-8700 and analyzed by fitting each peak in the spectrum. Once a successful fit was obtained, the parameters from each peak (height, center and width) and the background (slope and intercept) were used to compute the integrated area under each peak. From this, any X-ray line ratio from the spectrum could be computed. After analyzing all the samples at the three different energies and determining the X-ray line ratio values, the characteristic X-ray line ratios were plotted versus the aluminum overlay thickness.

4.2 THE SUBSTRATE TO OVERLAY X-RAY LINE RATIO

The results from the substrate X-ray line to the overlay X-ray line ratio are shown in Figures 11 and 12. Figure 11 is a plot of the experimentally determined copper L to aluminum $K\alpha$ X-ray line ratio versus the aluminum overlay thickness for 20, 25 and 30 keV electron bombardment. These results clearly show that the copper L to aluminum $K\alpha$ X-ray line ratio does not depend upon the accelerating electron energy and changes ≈ 85 percent over a thickness change of 4000 Å. Similarly, Figure 12 is a plot of the experimentally determined molybdenum L to aluminum $K\alpha$ X-ray line ratio versus the aluminum overlay thickness for 25 and 30 keV electron bombardment. As in the copper substrate, the molybdenum substrate L to overlay aluminum $K\alpha$ X-ray line ratio is also independent of the accelerating electron energy. This ratio demonstrates a large change, ≈ 86 percent, over a thickness change of 7000 Å.

4.3 THE SUBSTRATE L/ $K\alpha$ X-RAY LINE RATIO

The results from the substrate L/ $K\alpha$ X-ray line ratio are shown in Figure 13. This plot is of the substrate copper L/ $K\alpha$ X-ray line ratio versus aluminum

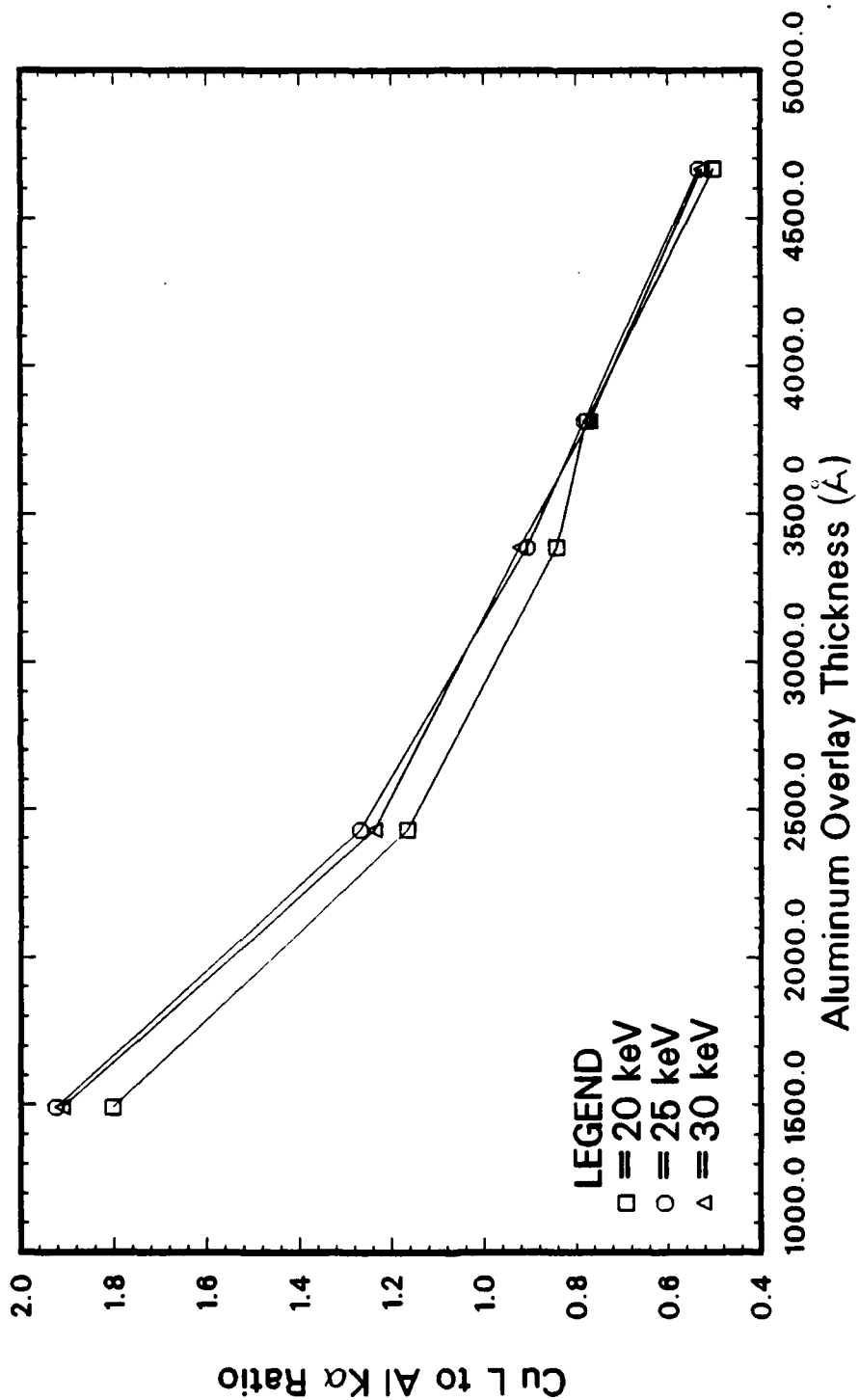


Figure 11. Measured copper L to aluminum K α X-ray line ratio versus the aluminum overlay thickness for 20, 25 and 30 keV electron bombardment.

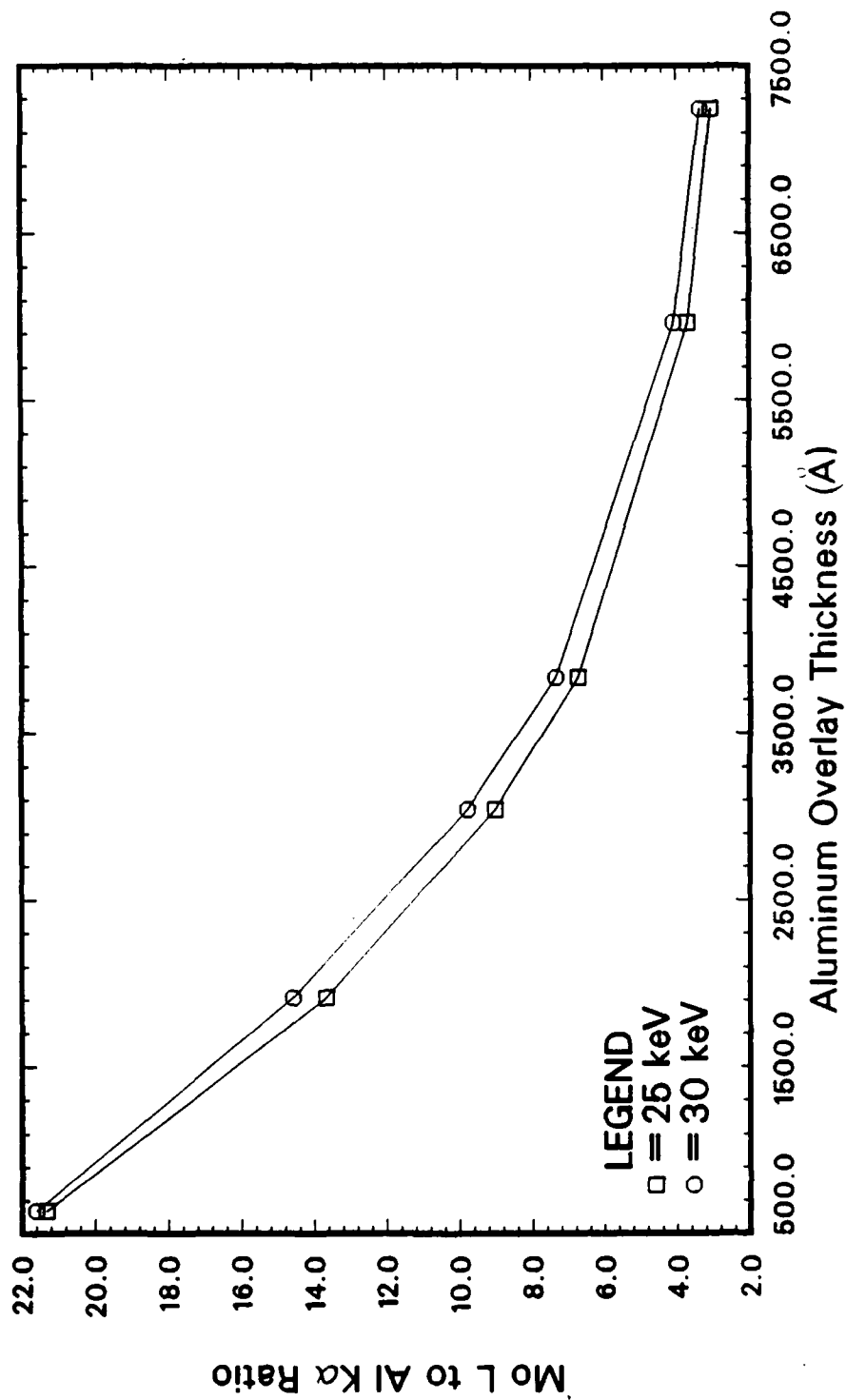


Figure 12. Measured molybdenum L to aluminum K α X-ray line ratio versus the aluminum overlay thickness for 25 and 30 keV electron bombardment.

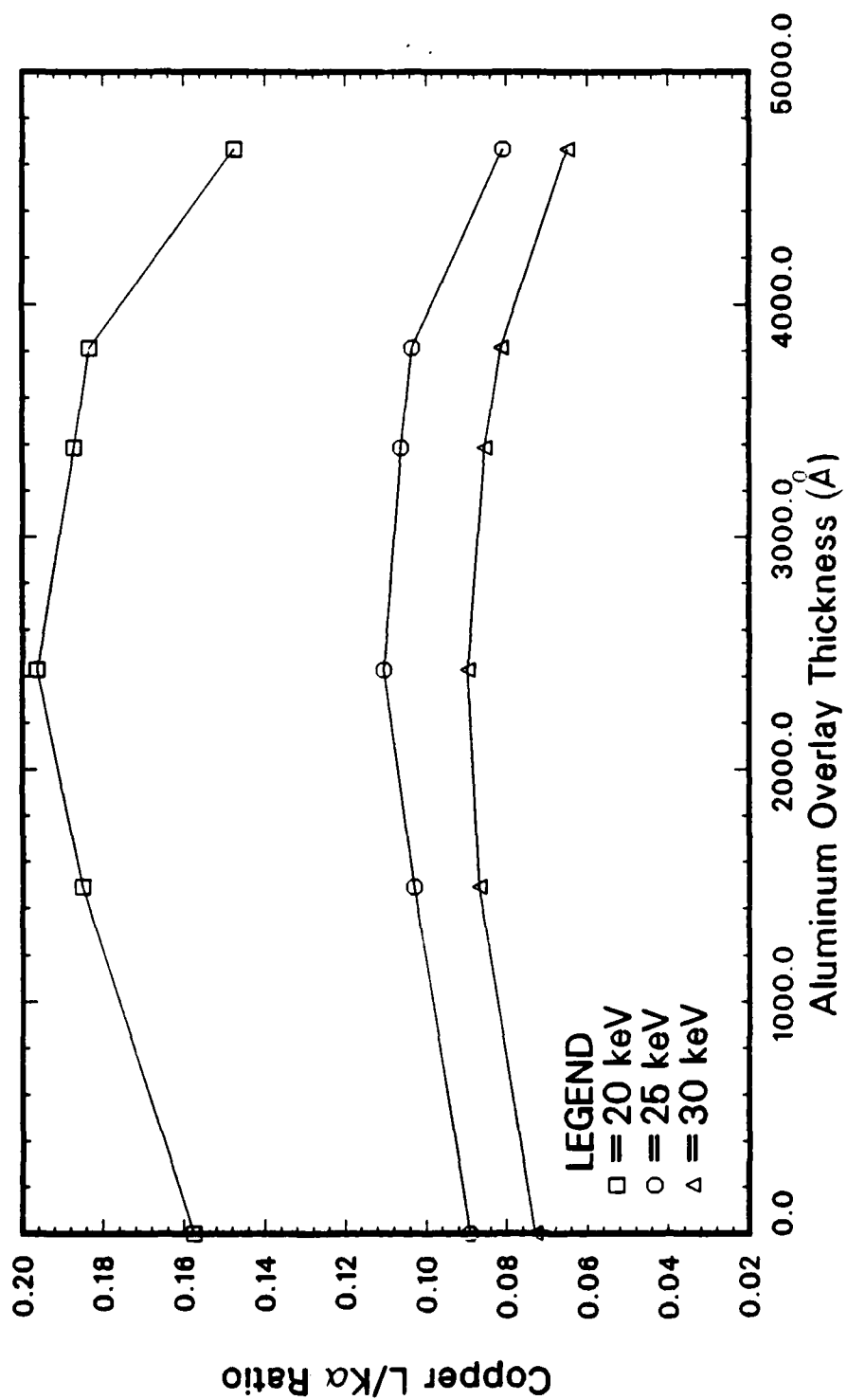


Figure 13. Measured copper L/K α X-ray line ratio versus the aluminum overlay thickness for 20, 25 and 30 keV electron bombardment.

overlay thickness for 20, 25 and 30 keV electron bombardment. It shows that the copper L/K α X-ray line ratio does depend on the accelerating energy of the electrons. Also, the data reveals that the copper substrate's L/K α ratio increases for thin overlays (< 2500 Å) and then begins to decrease for thicknesses > 2500 Å. Although the L/K α ratio differs for 20, 25 and 30 keV electron bombardment, all three experimental curves have the same shape and peak at $\approx$ 2500 Å. Experimental substrate L/K α X-ray line ratio data were not obtained from the molybdenum samples because the molybdenum K α peak's signal to noise ratio was too low to analyze.

5.0 DISCUSSION

5.1 THE SUBSTRATE TO OVERLAY X-RAY LINE RATIO

The experimentally determined and theoretical calculations of the substrate to overlay X-ray line ratio of the copper and molybdenum substrate samples, versus the aluminum overlay thickness are compared in Figures 14 and 15, respectively. Figures 14 and 15 show qualitative agreement between the experimental and theoretical curves. Both are proportional to $1/x$, where x is the overlay thickness. The theoretical curves for both the copper and molybdenum samples were calculated using Eq. 16, which was mathematically shown to be proportional to $1/x$.

The constant, K contained in Eq. 16 is the substrate's average yield per unit length times its X-ray line escape depth, divided by the overlay's average yield per unit length times its X-ray line escape depth. The copper L X-ray line escape depth is an order of magnitude smaller than that of the aluminum $K\alpha$ X-ray line escape depth. Moreover, because these two X-ray lines differ so little in energy (≈ 0.6 keV), their yields per unit length should also be about equal. This would suggest that K is ≈ 0.1 . However, the average yield per unit length is actually a function of dE/dx of the electrons traversing the film overlay. In the substrate material, assuming that the yield per unit length is equal to a constant is suitable since the substrate is thicker than the copper L X-ray line escape depth. But, for the thin film overlay, the aluminum thickness is less than the aluminum $K\alpha$ X-ray line escape depth. Therefore, the overlay's $K\alpha$ X-ray line yield will increase as a function of x because the electrons begin depositing more of their energy within the overlay. Thus, the actual value of K decreases as a function of overlay thickness, flattening the overlay to the substrate X-ray line ratio curve.

In Figure 14, K was adjusted until the theoretical ratio curve fit that of the experimentally determined ratio curve. This resulted in a K value of 30 for the copper substrate to aluminum overlay calculated ratio. This value of K is a little higher than expected. However, if the copper L X-ray line production is increased by another process other than electron bombardment, a higher value of K would be expected. The X-ray line enhancement from matrix effects has been reported for several layered and alloy targets [Refs. 9 and 10].

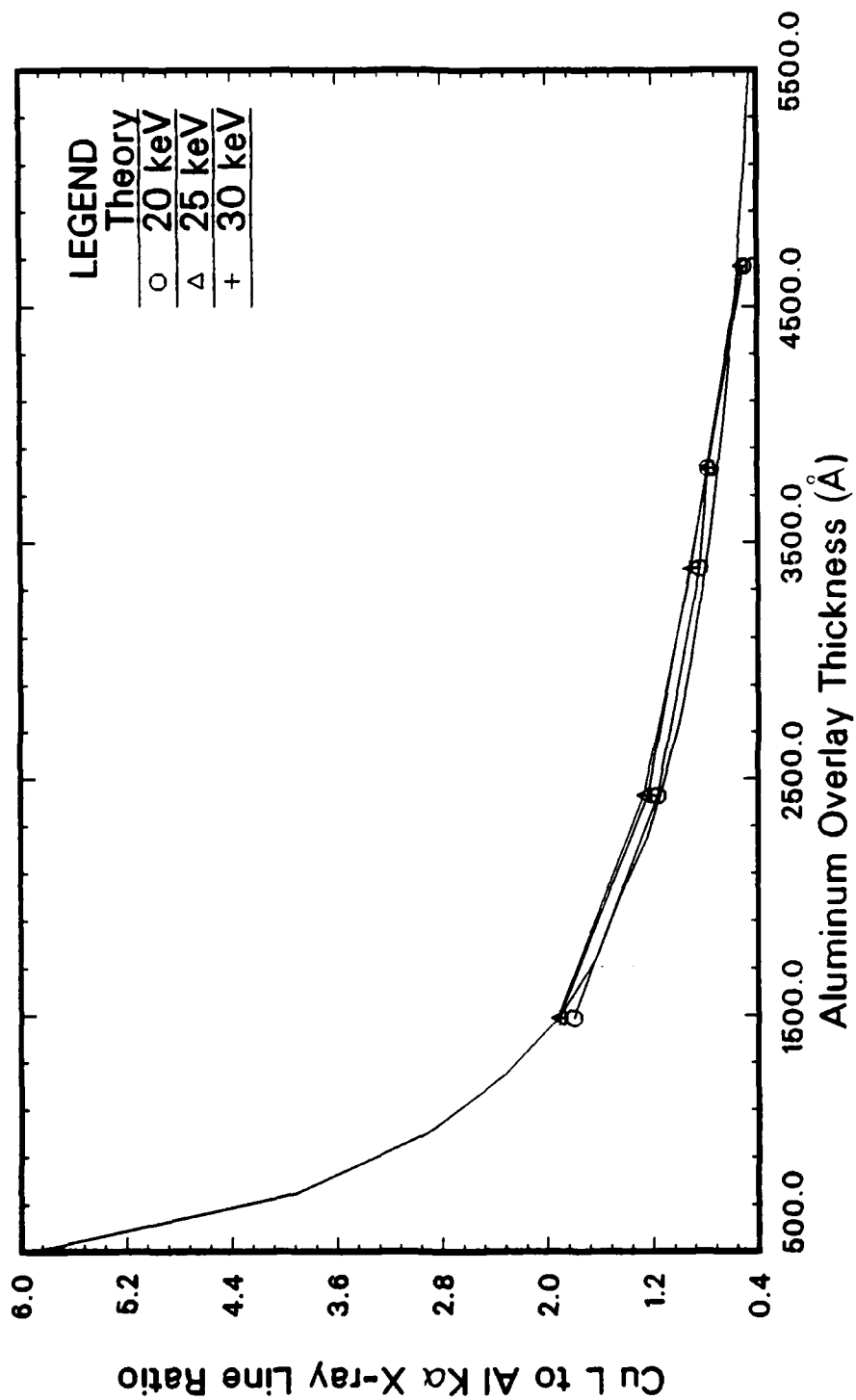


Figure 14. Theoretical and experimental curves of the copper substrate L to the aluminum overlay K α X-ray line ratio versus the aluminum overlay thickness. Theoretical value of the constant $K=30$ assumed.

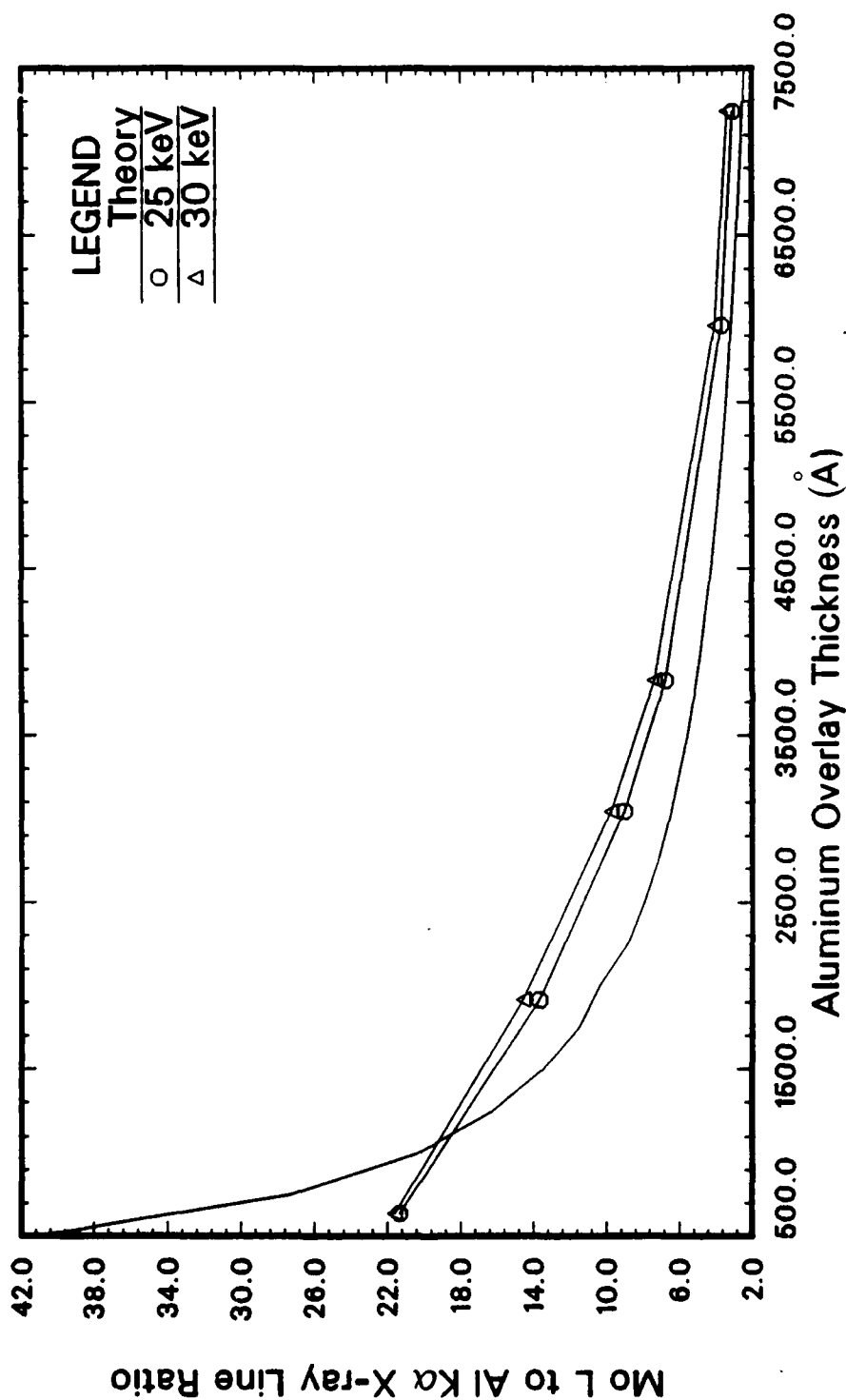


Figure 15. Theoretical and experimental curves of the molybdenum substrate L to the aluminum overlay K α X-ray line ratio versus the aluminum overlay thickness. Theoretical value of the constant $K=0.23$ assumed.

Matrix effects occur when an X-ray line of higher energy excites lower energy X-ray lines in the sample. In this case the aluminum $K\alpha$ X-ray line at 1.48 keV excites the copper L X-ray line of 0.9 keV in the substrate. The production rate for photon irradiation reported in Reference 11 can yield up to 0.5 additional X-ray photons per incident X ray of higher energy. This is a significant number when compared to that of $\approx 1 \times 10^{-4}$ X-rays per incident electron. This could easily explain the higher K value needed to fit the experimental data.

Similarly the theoretical molybdenum substrate L to aluminum overlay $K\alpha$ X-ray line ratio curve was fitted to the experimentally determined ratio curve. The resulting value of K was equal to 0.23. This was smaller than expected. However, the same matrix enhancement arguments apply here, only in reverse. In this case, the molybdenum substrate L x-ray line of 2.3 keV is higher in energy than that of the aluminum overlay $K\alpha$ X-ray line of 1.48 keV. Therefore, the molybdenum substrate L X-ray line will enhance the aluminum overlay $K\alpha$ X-ray line, decreasing K as a function of the overlay thickness.

In both cases the theoretical curve agreed qualitatively with that of the experimental data. Also, the values of K needed to fit the experimental data to the theory were reasonable. Moreover, the ratio was extremely sensitive to overlay thickness over a large range of values. These are both important conclusions that make the substrate to overlay X-ray line ratio technique a prime candidate for thin film measurements in industry.

5.2 THE SUBSTRATE L/ $K\alpha$ X-RAY LINE RATIO

The theoretical and experimental curves of the copper substrate L/ $K\alpha$ X-ray line ratio versus the aluminum overlay thickness for 30 keV electron bombardment is presented in Figure 16. The figure shows that the experimentally determined ratio versus overlay thickness does not agree with that of the theoretical ratio curve in that the former ratio increases with aluminum overlay thickness up to ≈ 2500 Å and then begins to decrease.

The explanation offered is that the copper substrate L X-ray line is being enhanced by the aluminum overlay $K\alpha$ X-ray line. Intuitively it can be seen that thin aluminum overlays attenuate the substrate's copper L X-ray line very

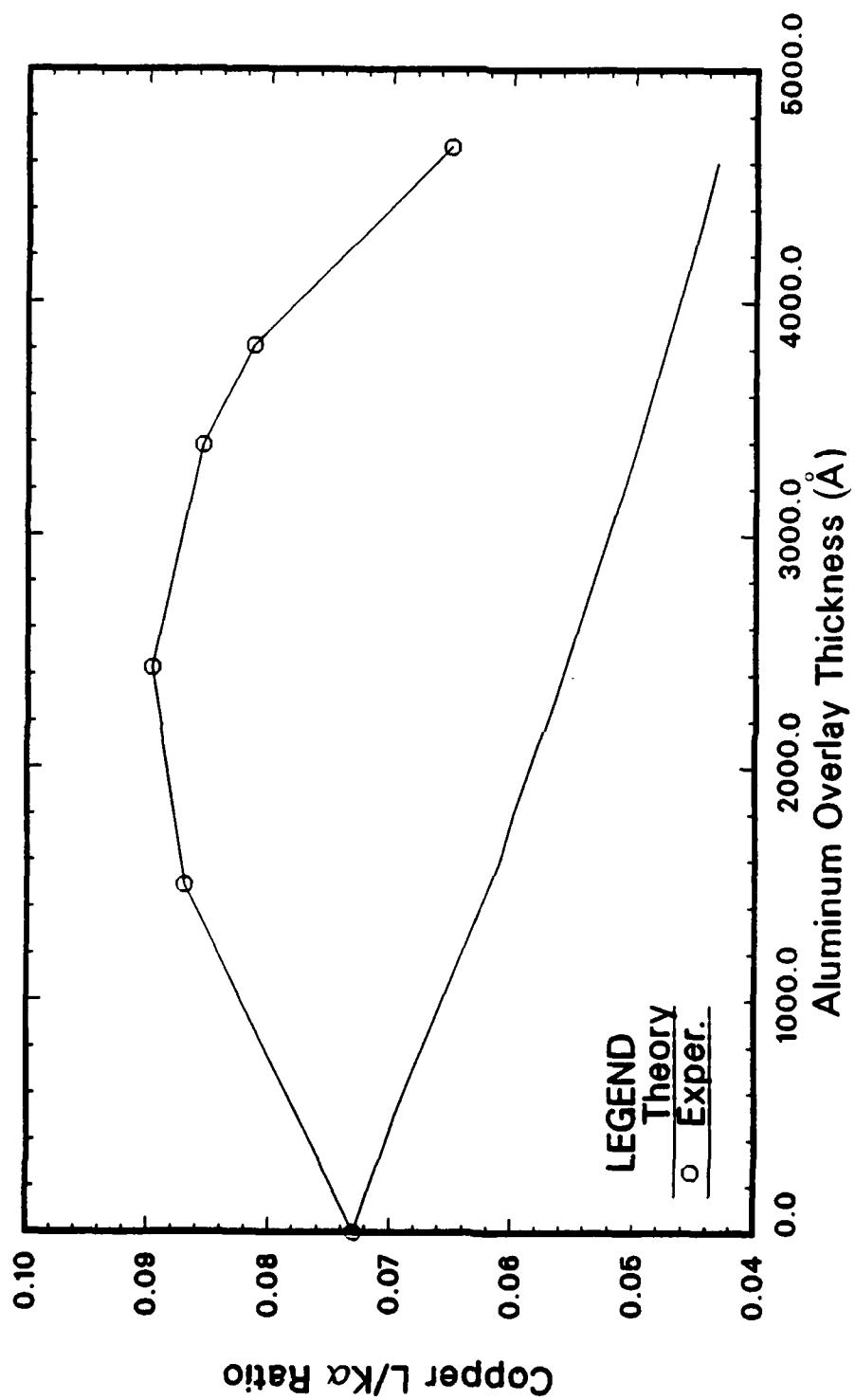


Figure 16. Theoretical and experimental curves of the copper substrate L/K α X-ray line ratio versus aluminum overlay thickness for 30 keV electron bombardment.

little, since attenuation is an exponential function. However, the large production yield (0.5 per incident photon) of copper L X rays from the bombardment of aluminum K α X rays will dominate for thin overlays as a function of x and electron dE/dx [Ref. 11]. The copper K α X rays are not affected by the aluminum overlay, except by attenuation. So, the copper L X-ray line increases and the copper K α line decreases. As the overlay material increases in thickness, the exponential attenuation term begins to dominate. Eventually, the copper L X-ray line is being attenuated at a faster rate than that of the higher energy copper K α X-ray line and the L/K α ratio begins to decrease.

5.3 SUMMATION

In summation, the substrate to overlay X-ray line ratio appears to be functional as a thin film thickness measurement technique. Matrix enhancement effects do not hinder this technique. Also, this ratio is sensitive to the overlay thickness (80 percent change in 7000 Å) and is independent of electron accelerating energy.

On the other hand, the substrate L/K α X-ray line ratio does not appear to be functional as a thickness measurement technique. The matrix enhancement of the substrate L X-ray line adversely affects this ratio for thin overlays. It is also dependent on the accelerating electron energy and yields two different thickness solutions for the same measured ratio.

6.0 RECOMMENDATION FOR FURTHER STUDY

Although room certainly exists for refinement of almost any portion of this work, one area seems particularly suited to further study. The substrate to overlay X-ray line ratio certainly needs to be investigated both experimentally and theoretically in detail before any industrial applications can be found. The data presented show that this ratio may be sensitive to thin film overlays and independent of the electron accelerating energy. Investigation into multiple target thicknesses and alloy overlays are natural follow-on research projects.

The substrate L/K α X-ray line ratio should also be studied, although the work reported here suggests that it is not usable as a thin film measurement technique. The matrix effects and how they change the ratio may be academically interesting. Also, there may be cases in which this ratio technique, with the proper combination of elements, may yield important information.

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