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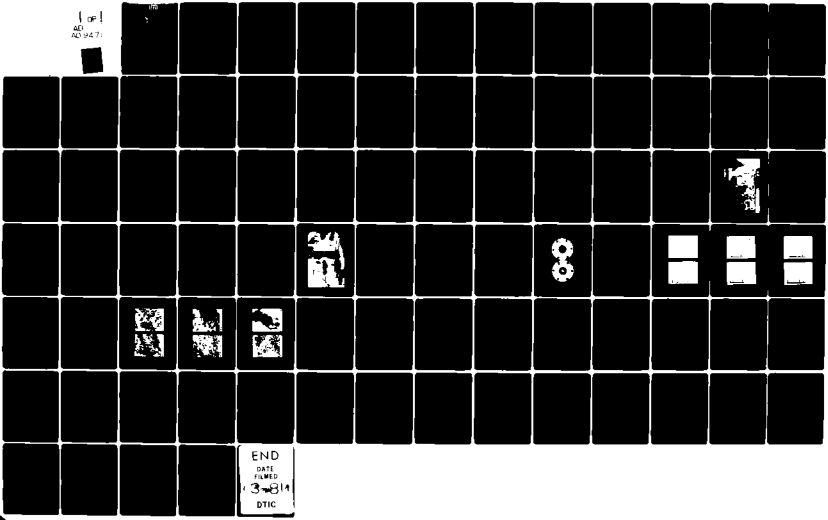

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INCOHERENT AND LASER PHOTODEPOSITION OF THIN FILMS

THESIS

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INCOHERENT AND LASER PHOTODEPOSITION OF THIN FILMS

THESIS

PRESENTED TO THE FACULTY OF THE SCHOOL OF ENGINEERING
OF THE AIR FORCE INSTITUTE OF TECHNOLOGY
AIR UNIVERSITY (ATC)
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS OF THE DEGREE OF
MASTER OF SCIENCE

BY

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Preface

This report summarizes three months of experimental effort devoted toward the production of thin films by the photodissociation of organometallic molecules containing the elements Zn and Se. This work was undertaken at the Air Force Weapons Laboratory to assess the potential of photodeposition as an alternate and greatly improved technique for producing high quality thin films suitable for high energy laser mirrors. Emphasis was placed on ZnSe since it is a very useful thin film for high energy laser mirrors in the infrared.

Two different approaches were used in the attempt to produce these thin films. Both techniques used the organometallic molecules, $Zn(CH_3)_2$ and $Se(CH_3)_2$, which have vapor pressures greater than 10 torr at room temperature (23°C). In the first technique, an Ar^+ 5145Å laser was frequency doubled to acquire the u-v laser emission at 2572Å. During experimentation, it was determined that the threshold wavelength for the photodissociation of both Zn- and Se- $(CH_3)_2$ was approximately 2420Å. Consequently, these laser photodeposition experiments were unsuccessful. As a second approach, an incoherent source emitting ultraviolet photons below 2420Å was used. This ensured that the photon energy was sufficient to dissociate these organometallics in a single step process that liberates free Zn and Se atoms which subsequently are deposited as a thin film on a substrate. The major objective of this thesis was accomplished; that is, ultraviolet photons were used to deposit a thin film of Zn, Se, and ZnSe from these organometallic molecules at room temperature.

I would like to acknowledge the many people who directly and indirectly helped in this undertaking. Thanks go to my advisor Dr. L.A. Schlie, who never ceased to amaze me in his diligence to successfully complete the research. Also, Major Stamm, who prepared me in my studies before the start of my experimental work at the Air Force Weapons Laboratory. I would like to mention two close associates at the AFWL, Mr. Robert Rathge and Lt Len Jusinski for their assistance. I also want to extend my appreciation to Mr. Willie Kunzler, Mr. Wayne Watson, Mr. Harold Thompson, Mr. Charles Miglionico, and A1C Virginia Bertrand for their diagnostical assistance and to Mr. Art Goodman for his photographic efforts. Special thanks also goes to Lt Col K.L. Jungling for his open minded support and encouragement of this thesis research. Appreciation is also extended to the Air Force in general and specifically the Materials Laboratory management at Wright-Patterson Air Force Base, Ohio, for sponsoring my master's education and to my direct supervisor Dr. Gary Denman for allowing me to conduct this work at the AFWL.

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Abstract

High purity Zn, Se, and ZnSe thin films (∿ 100 to 6000Å thicknesses) have been deposited on both quartz and sapphire substrates by using a Hg arc lamp u-v light source to photodissociate the organometallic molecules $Zn(CH_3)_2$ and $Se(CH_3)_2$. Large area depositions (∿ 1.5 cm diameter circles) have been produced, along with masked depositions created by selectively blocking the incoherent light source. Absorption measurements of these organometallic vapors from 0.2 to 20 microns indicates the possibility of producing ultra-high purity thin films by using simultaneously both a CO (5.6 - 5.9μ) and a CO_2 (10.6μ) laser in conjunction with a pulsed KrF (2480Å) in a highly selective two step photodissociation process. Such results offer the potential for a drastically new and greatly improved quality film plus an extremely well controlled alternative to the more conventional thin film deposition techniques such as thermal vacuum deposition, sputtering, and chemical vapor deposition.

INCOHERENT AND LASER PHOTODEPOSITION OF THIN FILMS

I Introduction

Since the development of high energy lasers, the Air Force has had a continued interest in improving the quality of thin films used for various types of optical elements (Ref 1). For example, the deposition of higher quality films on laser mirror substrates would be most valuable, especially to improve the energy damage threshold (joules/ cm^2) and the surface uniformity. Conventional techniques such as thermal vacuum deposition, chemical vapor deposition (CVD), and sputtering, are now employed to produce thin films (Ref 2,3). However, these alchemistical methods are not well controlled and can therefore deposit contaminants or impurities along with the desired products. For high energy laser mirrors, such impurities are known to produce hot spots for laser photon absorptions (Ref 4). This phenomenon is responsible for the energy damage threshold of the laser mirror's thin film coating. It is well documented that such a phenomenon permanently destroys the thin film on the high energy laser mirror. Therefore, a method of depositing thin films which results in the smallest quantity of absorbing impurities would benefit the Air Force. In this thesis, a new technique to possibly accomplish this important requirement is discussed. Results are presented demonstrating that thin films of Zn, Se, and ZnSe having thicknesses of 100 to 6000Å can be deposited on a quartz and/or sapphire (Al_2O_3) substrate by photodissociating the organometallic vapors of $Zn(CH_3)_2$ and $Se(CH_3)_2$.

Presently, there are three dominant techniques used to produce thin films (Ref 2,3). These are thermal vacuum deposition, sputtering and chemical vapor deposition (CVD). In the most common procedure thermal vacuum deposition, the evaporant is placed in a crucible and heated either directly or indirectly to produce a fairly significant vapor pressure. To obtain a reasonable thin film condensation rate, the evaporant and its holding crucible must be heated to an operating temperature necessary to produce a vapor pressure of 10^{-2} torr for the evaporant. For the majority of evaporants this corresponds to a temperature range of 1000 to 2000°C (Ref 5). In this technique, the major sources for film contaminants are the impurities intrinsic to the evaporant and the crucible holding the evaporant since the impurities have reasonable vapor pressures at these elevated temperatures. Another severe problem with this technique deals with the fact that the substrate being coated also becomes very warm from the radiant heat of the crucible holding the evaporants. Such an effect may drastically alter the figure of the mirror coating after the thin film coating is completed and then cooled to room temperature. Consequently, large stresses can be produced in the thin film once the substrate is cooled after the deposition process is completed.

In the sputtering technique, an inert gas discharge is maintained between two electrodes, one of which is a cathode made of evaporant to be sputtered. The other electrode (anode) is the substrate. During the discharge's operation, an inert gas is ionized and the ions collide with the cathode containing the material to be deposited. Under the influence of the voltage applied between the electrodes, the evaporant ions are accelerated toward the (anode) substrate and then deposited. In this technique, the major sources of contaminants in the film are impurities in the evaporant cathode and the inert gas.

The third technique for the production of thin films, CVD generally requires a source of the desired evaporants that flow into a vacuum. The sources are heated and mixed to promote the chemical creation of the evaporants. The evaporants are then flowed by a carrier gas to the substrate. The substrate is generally elevated above ambient temperature by the heat from the chemical reaction. For this procedure, the major sources of contaminants in the film arise from the impurities in the evaporant and carrier gas and reaction by-products of the evaporant and source.

From this brief discussion, it is quite obvious that none of these techniques provide a precise control over the depostion of the vapor on the substrate. Consequently, any alternative techniques that offer precise controllability of the deposition process are most attractive. A very interesting approach is to use photochemistry to selectively deposit thin films on substrates.

Photochemistry has been studied for many years. It involves the interaction of a quantum of light with a molecule to promote chemical reactions not attainable with the thermal energies of the chemical species mixed (Ref 6). The subbranch of photochemistry dealing with the production of free atomic species by photodissociation is used in the production of thin films useful for high energy laser mirrors. Here, complex molecules (specifically organometallics) are excited optically to repulsive electronic states to obtain free atoms. After such atoms are produced, they can chemically react to form certain molecules which are not easily obtained or precisely controlled by the more conventional processes such as the mixing of two different types of gases or liquids. In the work reported here, results are discussed in which, thin films of Zn, Se, and ZnSe have been deposited on both quartz and sapphire substrates by the photodissociation of the organometallic molecules $Zn(CH_3)_2$ and $Se(CH_3)_2$ with u-v ($\lambda < 2420\mathring{A}$) photons from an incoherent source. These results are very attractive in the search for a much improved and well controlled method of producing thin films useful for the dielectric reflecting surfaces of high energy laser mirrors or windows. Several of this method's attractive reasons are that: (1) the energy damage threshold (joules/cm^2) of mirrors may be drastically improved since through a two step selective laser dissociation of these organometallic molecules, very high purities may possibly be acquired; (2) much higher surface uniformities may be produced because the free atoms and/or molecules deposited are collisionally mixed at the high pressure (approximately one atmosphere at room temperature) used in this process (3) spatial variations of the elements in a thin film's characteristics and density for a compound can be varied by aperturing or attenuating the optical fluxes producing the deposition; and (4) it may be possible to produce mirror surfaces by polishing via spatially varying the deposition rate to fill the voids in the surface of the mirror.

The photodeposition of thin films consisting of a single atomic specie, has been previously reported by several authors (Refs 7-14). All of these depositions have been produced by incoherent sources except for one group (Ref 13). In all of these depositions, the films have been very small in area (about 1 mm^2) and thickness (~ 100Å) and consisted of only one atomic specie. The work presented here is a very large step forward since two atomic species have simultaneously been deposited and large area depositions (~ 1.5 cm diameter areas) have been produced with thicknesses of up to 6000Å. Furthermore, in Section IV, techniques and measurements are shown how selective laser excitation may be used to produce extremely high purity thin films via a two step laser sequential process. The successful development of this type of thin film deposition technology may produce a quantum jump in the production of thin films for use with high energy laser mirrors.

In Section II, the theoretical approach will be discussed. Next, in Section III, the experimental procedure will be described. Then in Section IV, all of the experimental results will be discussed and in Section V conclusions will be made. Finally, in Section VI, the recommendations for future work will be outlined.

II Theoretical Approach

In this section, the theoretical basis for the production of thin films of Zn, Se, and ZnSe by photodeposition is discussed. First, the spectroscopy of the $Zn(CH_3)_2$ and $Se(CH_3)_2$ organometallic molecules is described. These molecules, which have vapor pressures in excess of 10 torr at room temperature, are the sources for the free Zn and Se atoms. Secondly, the physical chemistry of these organometallic molecules will be addressed. Then, finally a brief description of the important phenomena dealing with the surface physics of thin films will be outlined as these phenomena relate to this photodeposition scheme.

(A) Spectroscopy of Zn- and Se- dimethyls

The dominant reason for employing the organometallic gases of dimethyl zinc, $Zn(CH_3)_2$, and dimethyl selenium, $Se(CH_3)_2$, as a source of Zn and Se atoms is that these gases have high vapor pressures (greater than 10 torr) at room temperature. In the next section, these vapor pressures are discussed. To liberate the Zn and Se by photons, the spectroscopy of these molecules must be known. Thompson and Linnett (Ref 15-17) have experimentally measured the ultraviolet absorption bands for these molecules plus many other polyatomic molecules containing methyl and ethyl radicals. They reported continuous absorption bands for $\lambda < 2600\text{Å}$ which peaks around 2000Å for $Zn(CH_3)_2$. No ultraviolet data for $Se(CH_3)_2$ was reported. However, they do report data for $S(CH_3)_2$. During the original phases of this work it was assumed that $Se(CH_3)_2$ had an absorption band behavior similar to $S(CH_3)$ since S and Se are both in the same family of the Periodic Table, Group VI A. Data presented in Section IV corroborates this assumption, with the exception that the threshold wavelength is 2420Å not 2450Å (Ref 17:120-121). Unfortunately, no absolute measurements (cross sections) were given by Thompson. In Section IV-B, measurements are presented indicating that $\sigma_d \simeq 10^{-19}\ cm^2$ and that the threshold wavelength for the photodissociation of both $Zn(CH_3)_2$ and $Se(CH_3)_2$ is 2420Å. This value for $Zn(CH_3)_2$ is different from the value of 2600Å previously reported. The newly established value accounts for the large amounts of ultraviolet scattering by these large organometallic molecules.

As discussed in the introduction, it will be necessary to operate in a two-step mode process in order to produce extremely pure thin films for advanced high energy laser mirrors. To accomplish this goal, it is essential to know the infrared absorption spectra of both Zn- and Se- dimethyl. Much work has previously been done in this area (Ref 18-26).

These results demonstrate that there exists significant and structured absorption in the region from 1.5 to 11 microns. However, the magnitudes for the absorption cross sections have not been measured and published to this date. Such data is reported for the first time in Section IV-B.

In Figure 1, the pertinent potential energy curves for either $Zn(CH_3)_2$ or $Se(CH_3)_2$ are shown. The well depths are approximately 60 kcal (Ref 17:128) while the repulsive curve relative to the bottom of the well is 110 kcal (Ref 27). Free Zn or Se is produced by a single step photoexcitation of the organometallic molecules to a repulsive state that subsequently dissociates into a free atom and two methyl radicals. The cross section for this process is given in Figure 25 of Section IV-B. In Section III-C, it is stated that the Hg arc lamp u-v output power below the threshold wavelength of 2420Å required for the photodissociation is only 10 watts. This is distributed non-uniformly over an area having a diameter of 2 cm which gives a useful u-v intensity, I, of only 3.2 watts/cm^2. Using the single step u-v photodissociation cross section α_d (see Fig 25) of 10^{-19} cm^2 makes the dissociation rate R_d of $Zn(CH_3)_2$ or $Se(CH_3)_2$ molecules to be only

$$R_d = \sigma_d \left(\frac{I}{h\nu} \right) \qquad (1)$$

$$= 0.39/\text{sec}$$

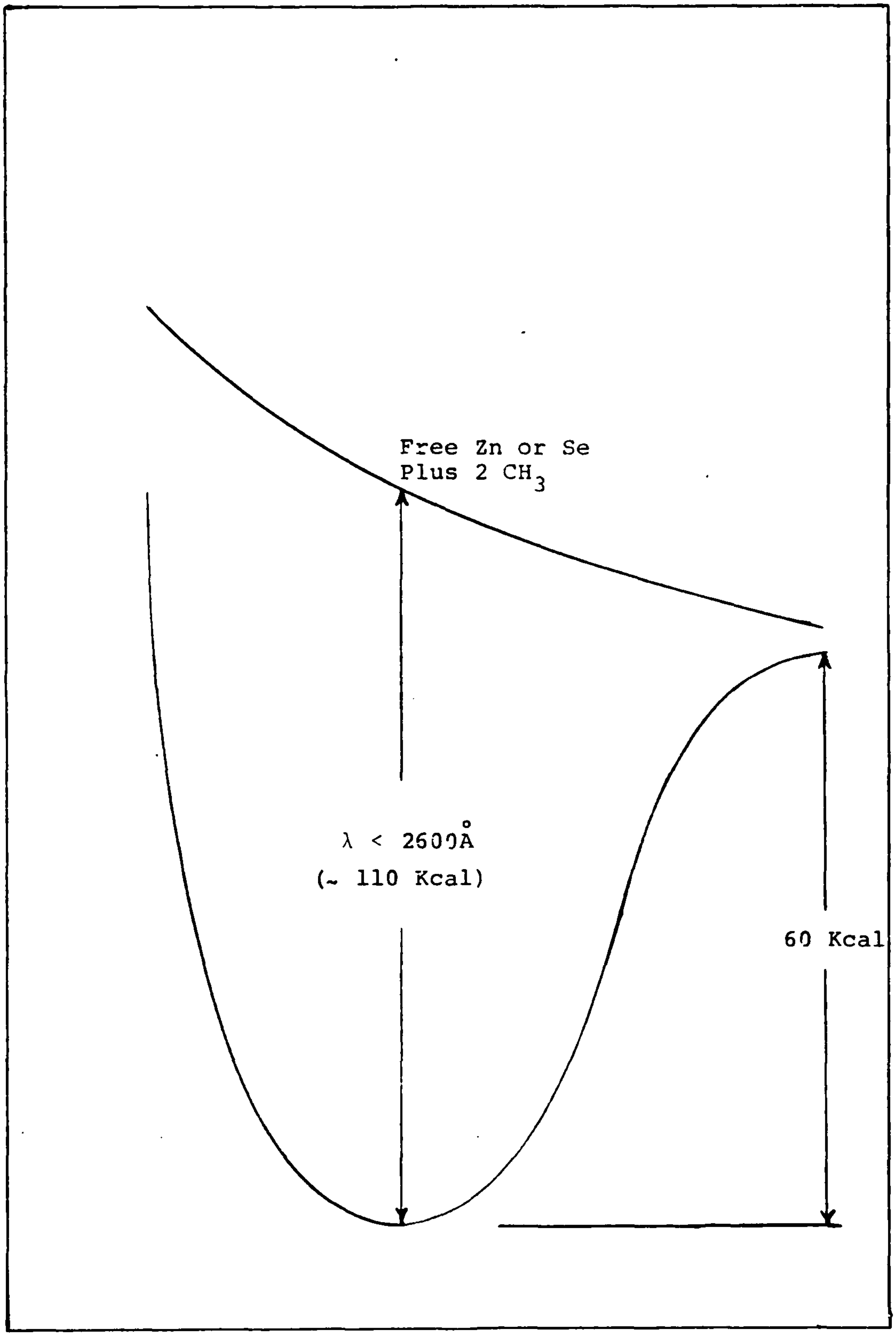


Figure 1. Potential Energy Curve for $Zn(CH_3)_2$ and $Se(CH_3)_2$

where $h\nu$ corresponds to the energy of a 2420Å photon. This low rate is due to the use of an incoherent light source. Any future work done with the laser will give an enhanced rate of easily 10^4 to 10^6 due to the much higher available intensities. The rate cited in Eq (1) is the maximum rate at which Zn and Se atoms can be deposited with the Hg arc lamp. In practice a much lower deposition rate would be expected since many processes are required to occur for a free element to be deposited on a surface. This is discussed in Section II-C.

Since the potential energy curve is a multi-dimensional surface, it will have many vibrational modes. These transitions account for the vibrations between the Zn or Se atoms and the methyl radicals and between the C and H atoms in the methyl radical. The exact transitions are discussed in Section IV-B. The cross section for these processes can then be used to calculate the pumping rates for excitation using different IR laser sources having different intensities.

(B) Physical Chemistry of Zn- and Se- $(CH_3)_2$ Organometallics

The most attractive feature of organometallics is that they have high vapor pressures at room temperature. In

Figure 2, the saturated vapor pressure of both $Zn(CH_3)_2$ and $Se(CH_3)_2$ are shown. For $Zn(CH_3)_2$ the vapor pressure is approximated by the relation (Ref 25:793)

$$\log_{10} p(\text{torr}) = 7.52 - \frac{1486}{T(^\circ K)} \qquad (2)$$

and for $Se(CH_3)_2$, the relation is (Ref 28)

$$\log_{10} p(\text{torr}) = 7.98 - \frac{1678}{T(^\circ K)} \qquad (3)$$

where the pressure, p, is given in torr and the temperature, T, is expressed in degrees Kelvin.

In assessing the organometallics, the physical configuration of its atoms is important. Such knowledge enables one to assess its chemical stability and spectral behavior, particularly in the infrared and longer wavelength region of the spectra that are caused by vibrational and rotational effects. Such information is shown in Figures 3 and 4 for both $Se(CH_3)_2$ (Ref 22) and $Zn(CH_3)_2$ (Ref 29).

In the experimental handling and use of the organometallics, the chemical aspects become very important. Both of these organometallics are known to explode instantaneously when exposed to air (Ref 30). In addition, they are both very reactive with H_2O vapor. $Zn(CH_3)_2$ is

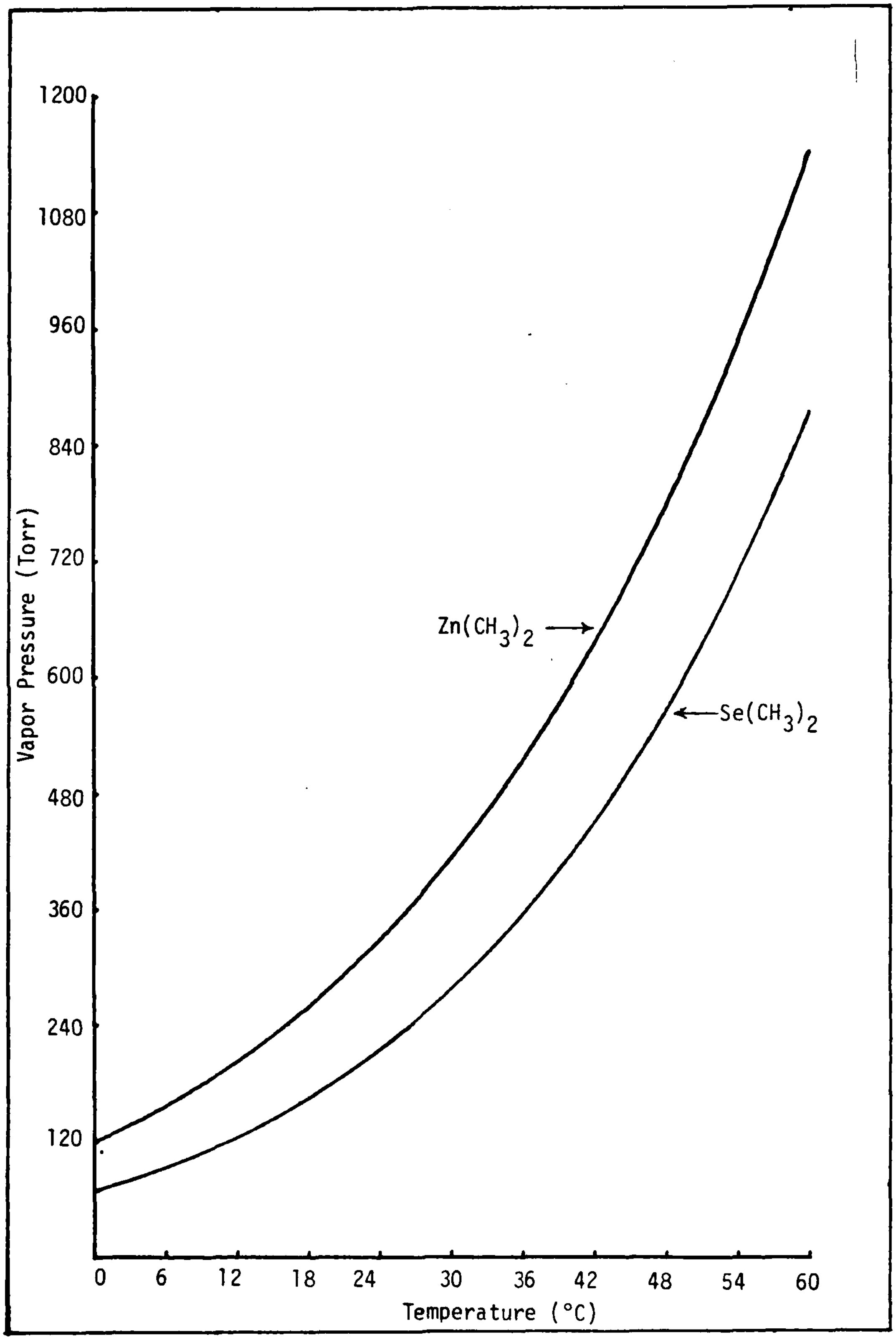


Figure 2. Saturated Vapor Pressures of the Organometallic Molecules of $Zn(CH_3)_2$ and $Se(CH_3)_2$

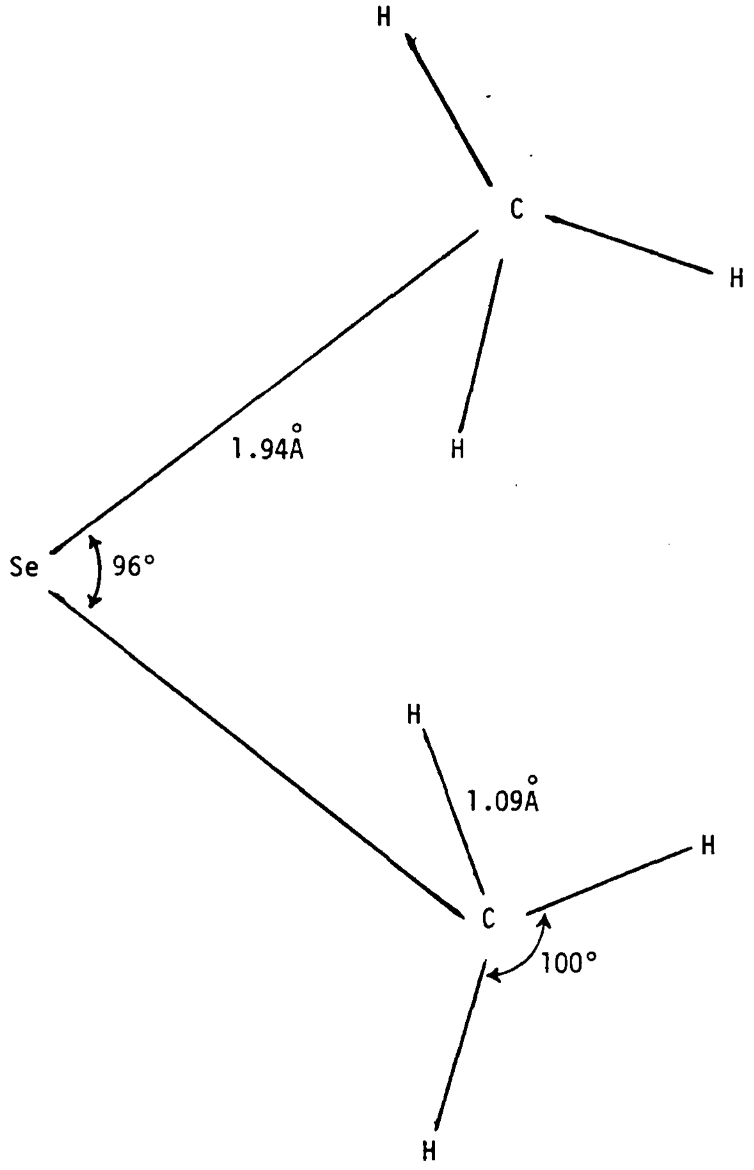


Figure 3. Physical Configuration of $Se(CH_3)_2$

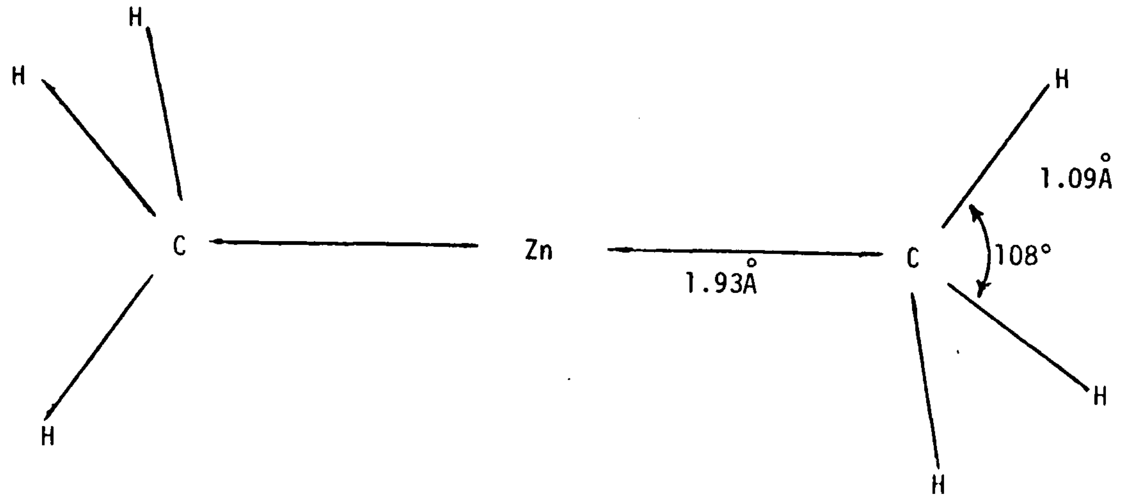


Figure 4. Physical Configuration of $Zn(CH_3)_2$

also extremely pyrolytic while $Se(CH_3)_2$ is very toxic. It was these physical characteristics that required extreme safety precautions to be implemented while the experiments were being conducted.

(C) Surface Physics of Thin Films

Generally, a thin film is made by depositing the film material atom by atom onto a substrate. The best understood process of depositing a film is that of condensation from the vapor phase. The film condenses on the substrate by transforming from a gas into a liquid or solid. In order to describe some of the physical phenomena pertinent to the surface physics of thin films, the approach discussed in the Handbook of Thin Film Technology (Ref 3) and Physics of Thin Films (Ref 31) is followed.

The initial step in depositing a thin film is the impingement of vapor atoms on the substrate. The atom can proceed along one of three courses after encountering the substrate. It can absorb and permanently adhere to the substrate. Alternatively, it can adsorb and re-evaporate after a period of time or simply "bounce off" the substrate.

Vapor atoms usually arrive at the substrate's surface with energies much greater than KT_s, where k is Boltzman's constant and T_s is the substrate's temperature. The value of the thermal accommodation coefficient, α_T, defines the course a vapor atom takes after encountering the substrate. The coefficient is defined by the following:

$$\alpha_T = \frac{E_v - E_r}{E_v - E_d} = \frac{T_v - T_r}{T_v - T_d} \qquad (4)$$

where

E_r = desorbed atom's energy before equilibration with the substrate

E_v = vapor atom's incident kinetic energy (dependent on initial position on repulsive curve)

E_d = desorbed atoms's energy after it equilibrated with substrate

T_v, T_r, and T_d = the corresponding temperatures

The α_T coefficient's value ranges from zero to one. When α_T is one, the vapor atom will equilibrate rapidly enough with the substrate so that it is absorbed. Here, the atom loses all its excessive energy and its energy state is then determined by the substrate's temperature. If α_T is less than one the vapor atom will rebound without having lost all of its incident energy to the substrate. The zero value is for the case of the atom's elastic reflection from the substrate.

The adsorbed atoms may remain on the surface for a time of τ_s, which is given by:

$$\tau_s = \frac{1}{\gamma_a} \exp \frac{\Delta G_{des}}{kT_a} \qquad (5)$$

where

γ_a = frequency at which the adsorbed atom attempts to desorb, and is thus equated to its vibrational frequency ($\sim 10^{14}$ Hz)

ΔG_{des} = activation energy for the desorption process

k = Boltzman's constant

T_a = temperature of the atom (generally between that of the evaporation source temperature and that of the substrate)

The absorbed atom which has not fully accommodated has retained an excess of energy. Because of this energy and the thermal energy from the substrate the atom moves over the surface. This movement is called migration or surface diffusion. During the course of its diffusion the atom can encounter another atom to form a pair. The pair will have a lower reevaporation probability then a single atom will have.

Nuclei are formed when several adsorbed atoms form a small cluster. This process of cluster formation is termed nucleation. A supersaturation ratio greater than one is necessary for nucleation to occur. The supersaturation ratio is the ratio of flow of the impinging atoms to their flow of reevaporation. The reevaporation flow is determined by the equilibrium pressure of the evaporant vapor at the temperature of the substrate. The process of enlargement of the nuclei to form a coherent film is called growth. Often both growth and nucleation simultaneously occur during a film deposition.

When a substrate under impingement of condensate atoms is observed with an electron microscope, the first evidence of condensation is nuclei of fairly uniform size. The smallest nuclei detected have a size of 20 to 30 Å. Growth of nuclei are three dimensional but, growth parallel to the substrate is greater than normal to it. This is probably due to the migration of atoms on the surface rather than by direct impingement from the vapor phase. The nuclei continue to grow and these islands of atoms begin to coalesce. Following the coalesence is the formation of long, irregular, and narrow channels. Secondary nucleation occurs in these channels until a continuous film results.

In addition to the surface physics discussed above, there also exists the formation of the molecule ZnSe from the free Zn and Se atoms. The physics of this formation intimately involves chemical thermodynamics. However, this is beyond the scope of this thesis.

III EXPERIMENTAL PROCEDURE/Set-Up

(A) Gas Filling/Mixing System

Since both of the organometallic compounds $Zn(CH_3)_2$ and $Se(CH_3)_2$ react violently with air and moisture, a high quality vacuum system was built (Ref 30). Figure 5 shows a diagram of the gas filling/mixing system used to store and transport the organometallic compounds. All valves and piping used in the vacuum station were type 304 stainless steel since it is known to have excellent compatibility with the organometallics (Ref 32). Technical grade acetone was used to wash out all vacuum components prior to their use in the vacuum station. The vacuum station was connected to a Welch turbomolecular pump capable of pumping down to an ultimate pressure of 10^{-6} torr. For the pressure measurements, conventional Wallace-Tiernan pressure gauges previously calibrated against known standards were used. A leak detector was also used to assure that a very low leak rate existed for this vacuum system (10^{-9} cm^3/sec). Due to the toxicity of $Se(CH_3)_2$, the gas filling part of the vacuum station was enclosed in a fume hood in order to insure adequate safety. Prior to connecting the vacuum system to the Zn- and Se- $(CH_3)_2$, the entire system was baked out to 150°C under vacuum to assure no H_2O remained

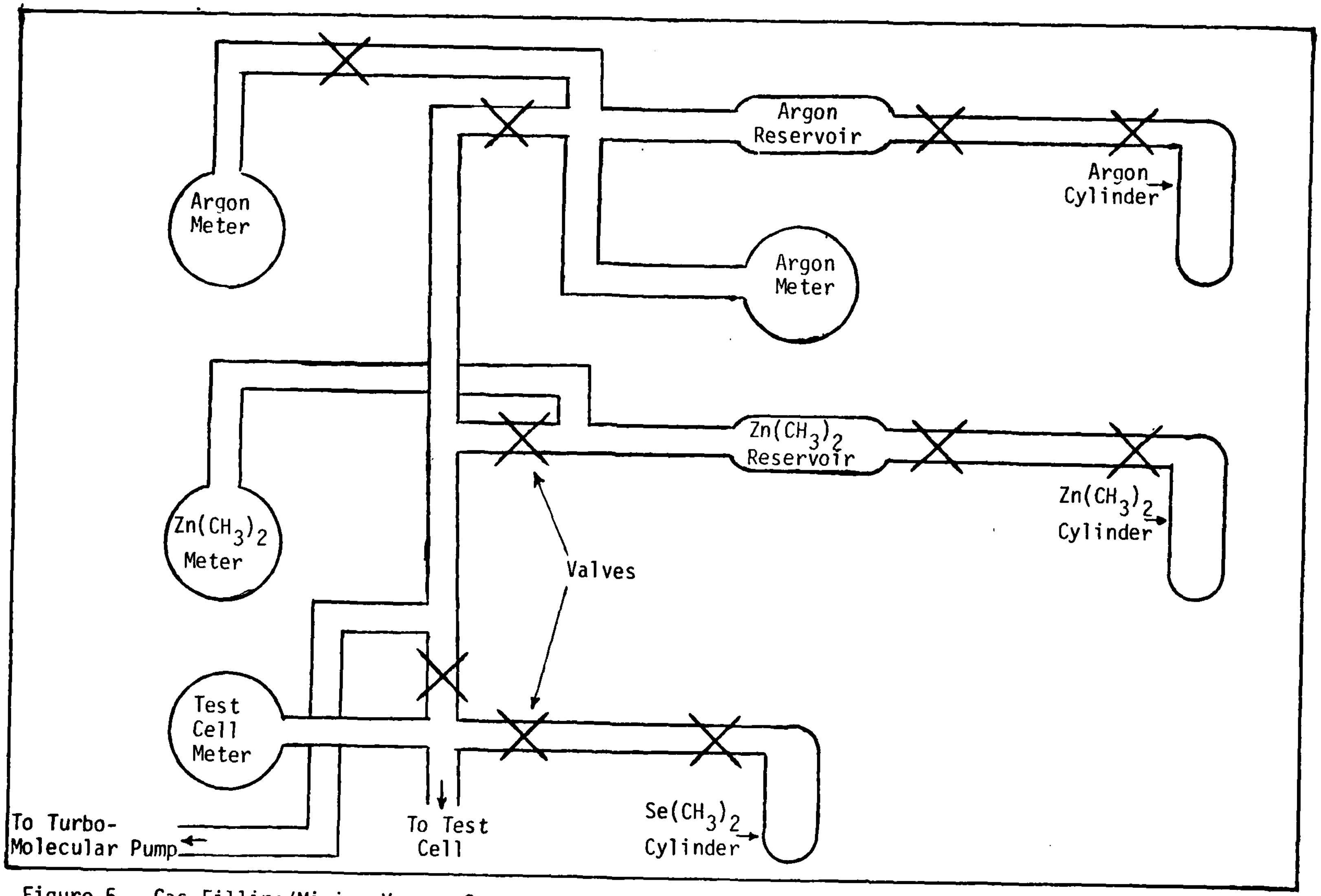


Figure 5. Gas Filling/Mixing Vacuum System

in the system. This was very important since $Zn(CH_3)_2$ violently reacts with H_2O vapor (Ref 30).

For safety reasons a lab coat, rubber gloves, and a plastic face shield were worn during the handling and the connection of the organometallic containers to the gas filling/mixing system. Both a carbon dioxide and dry chemical fire extinguisher were on hand in case a fire was initiated by the compounds.

The dimethylzinc was acquired from Alfa Products (Ventron Div) and was supplied as a liquid in a stainless steel cylinder. The cylinder contained 25 grams of the liquid with a purity of 99.9%. The dimethylselenide was also purchased from Alfa Products. It was supplied as a liquid in glass ampules containing five grams of liquid with a purity of 99.9%. To introduce the dimethylselenide's vapor into the gas filling/mixing system a "crunch tube" was fabricated as shown in Figure 6. The tube was made of stainless steel. A stainless steel Nupro valve was cut in order to expose its plunger. The valve was then welded to the tube. When the valve was closed, the plunger moved into the cylinder and crushed the glass ampule of dimethylselenide. In filling the "crunch tube", the dimethylselenide ampule was placed in a glove box which had been purged with argon gas for 4 hours. The argon gas provided

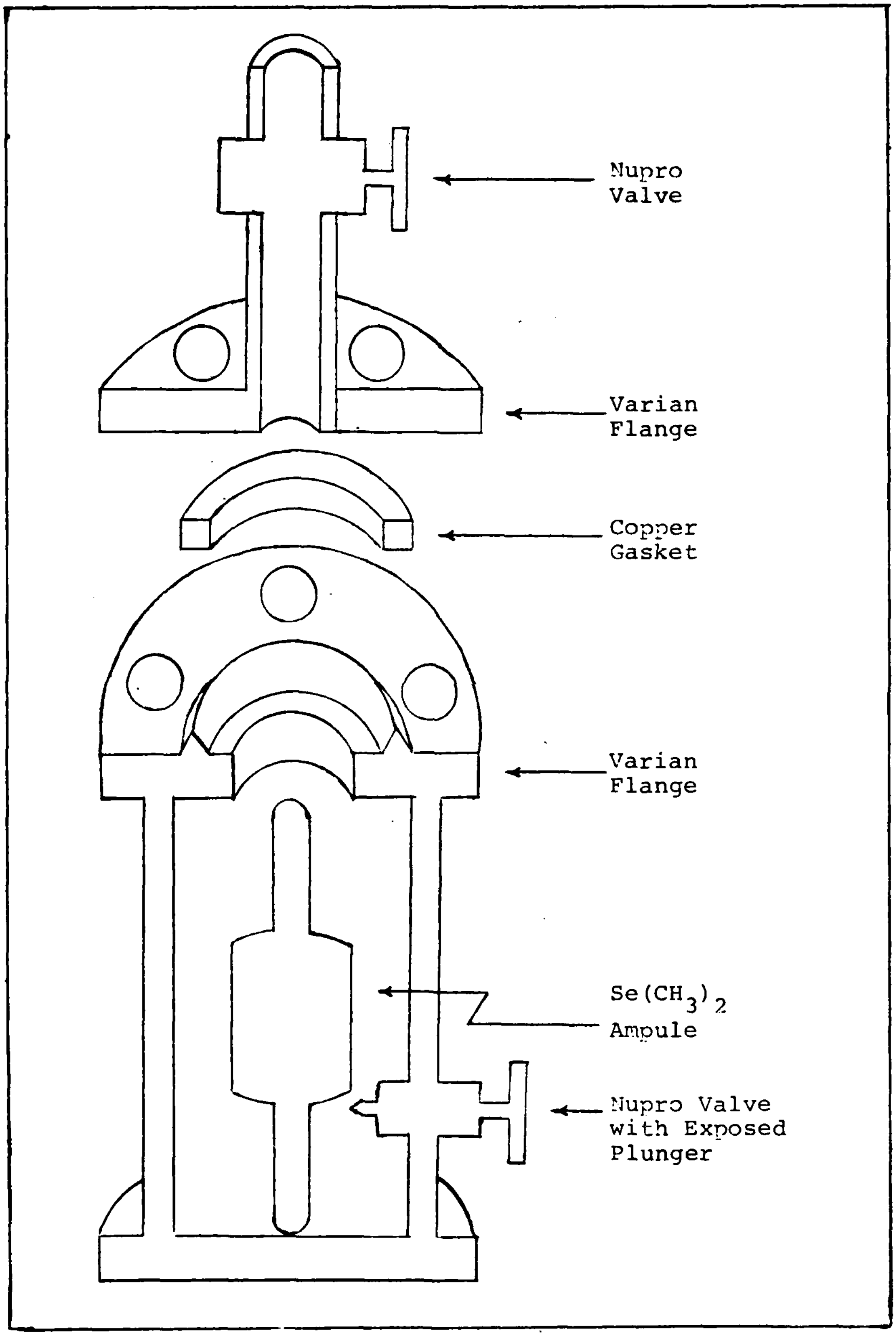


Figure 6. "Crunch Tube" used with $Se(CH_3)_2$

an inert atmosphere in case the ampule was broken. While in the glove box, the ampule was rinsed with technical grade acetone to remove contaminates and then placed in the "crunch tube". The tube was then joined to a standard Varian flange which had a Nupro valve connected to it. The valve on the Varian flange was closed (see Figure 6). The "crunch tube" then contained the dimethylselenide ampule in an argon atmosphere. Then the tube was removed from the glove box and connected to the gas filling/mixing system. The valve on the Varian flange was opened and the turbomolecular pump removed the argon from the tube. At this point, the cylinder was under a vacuum and its connections were leak checked with technical grade acetone. The final check to assure the cylinder was vacuum leak tight was valving the turbomolecular pump closed.

The cylinder of dimethylzinc was also uncapped in a glove box. The glove box had argon gas flowing through it for approximately four hours before the cylinder was uncapped. This was done to assure that any trapped organometallic vapors would not be exposed to air. The argon gas diluted any vapors and was flowed from the glove box through a blower to the outside atmosphere. The cylinder's valve was checked to assure that it was closed before being uncapped. After the cylinder was uncapped, stainless steel

Swagelock fittings were attached. The cylinder was then removed from the glove box and connected to the gas filling/mixing system. These new connections were checked for leaks to insure vacuum integrity to better than 10^{-6} torr, the ultimate capability of the vacuum system.

Once the vacuum system plus gas supplies (Zn- and Se-$(CH_3)_2$ and research grade Ar) were in operational order, the test cells were checked for vacuum integrity. Each was made from a standard varian double sided flange which had a quartz window on one side and a sapphire window on the other. In Figure 7, a detailed drawing illustrates the construction of the test cell. The test cells were filled using various gas mixtures for the system shown in Figure 5. High purity argon (99.999%) gas was used as the inert gas.

(B) Laser Photodeposition Set-Up/Procedure

The optical set up for the laser photodeposition is shown in Figure 8. Figure 9 is a photograph of the actual experimental arrangement. An argon ion laser having a cw power of 5 watts was tuned to 5145Å using a fused silica quartz prism. Next, the beam was propagated into a fume hood using various turning mirrors to assure that the direction of the laser radiation's electric vector was horizontally polarized. This was necessary to insure

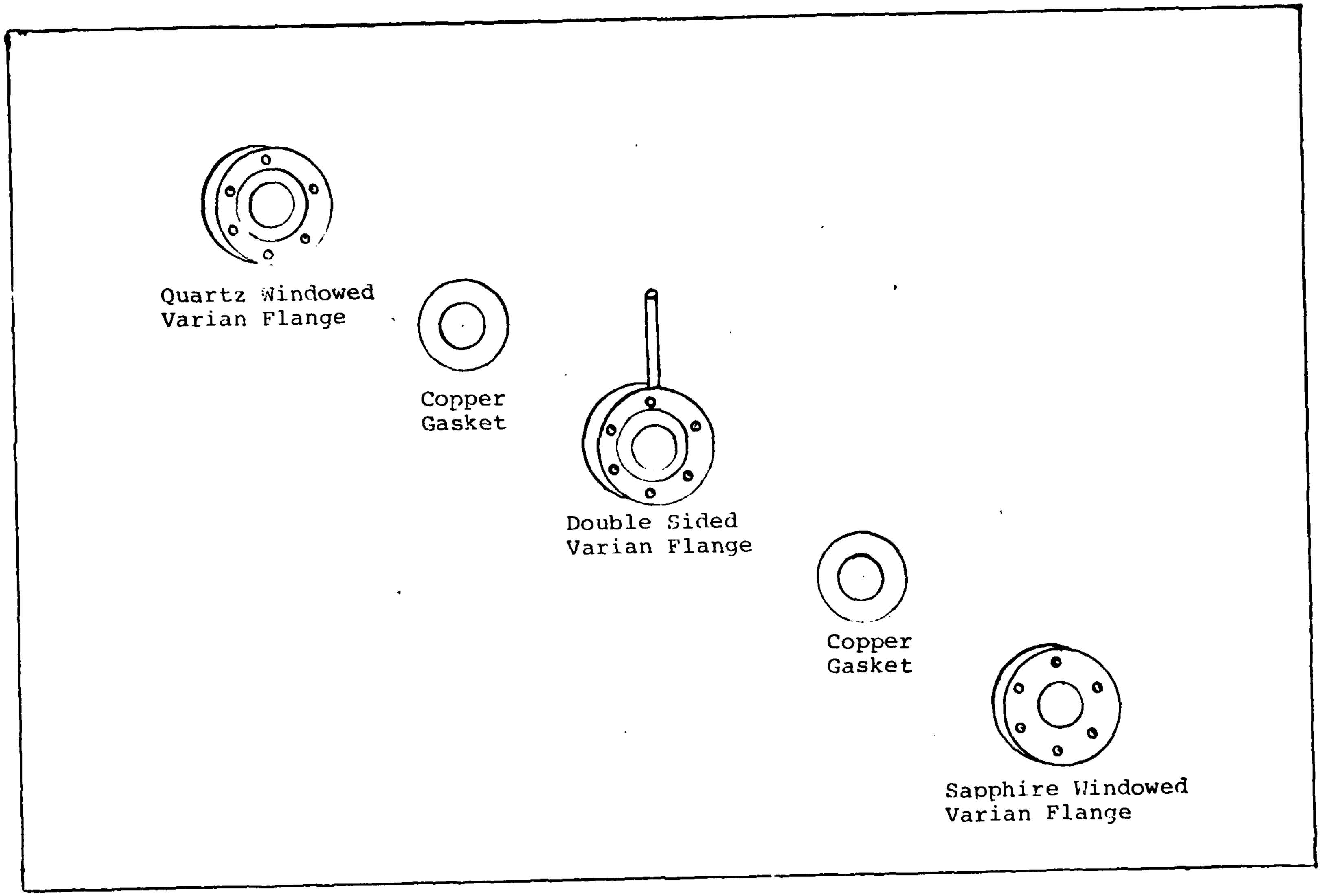


Figure 7. Test Cell Construction

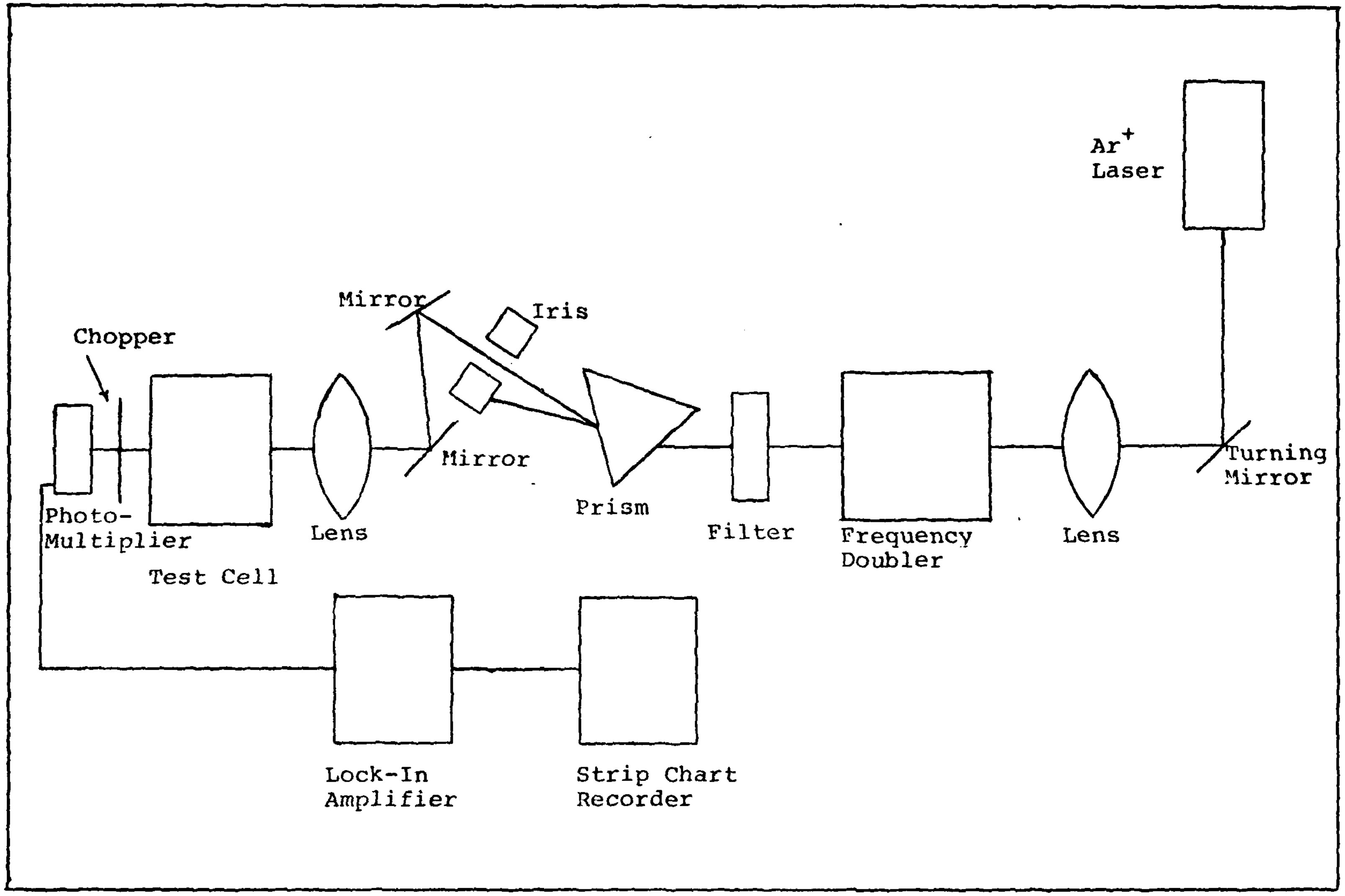


Figure 8. Optical Set-up for Laser Photodeposition Experiment

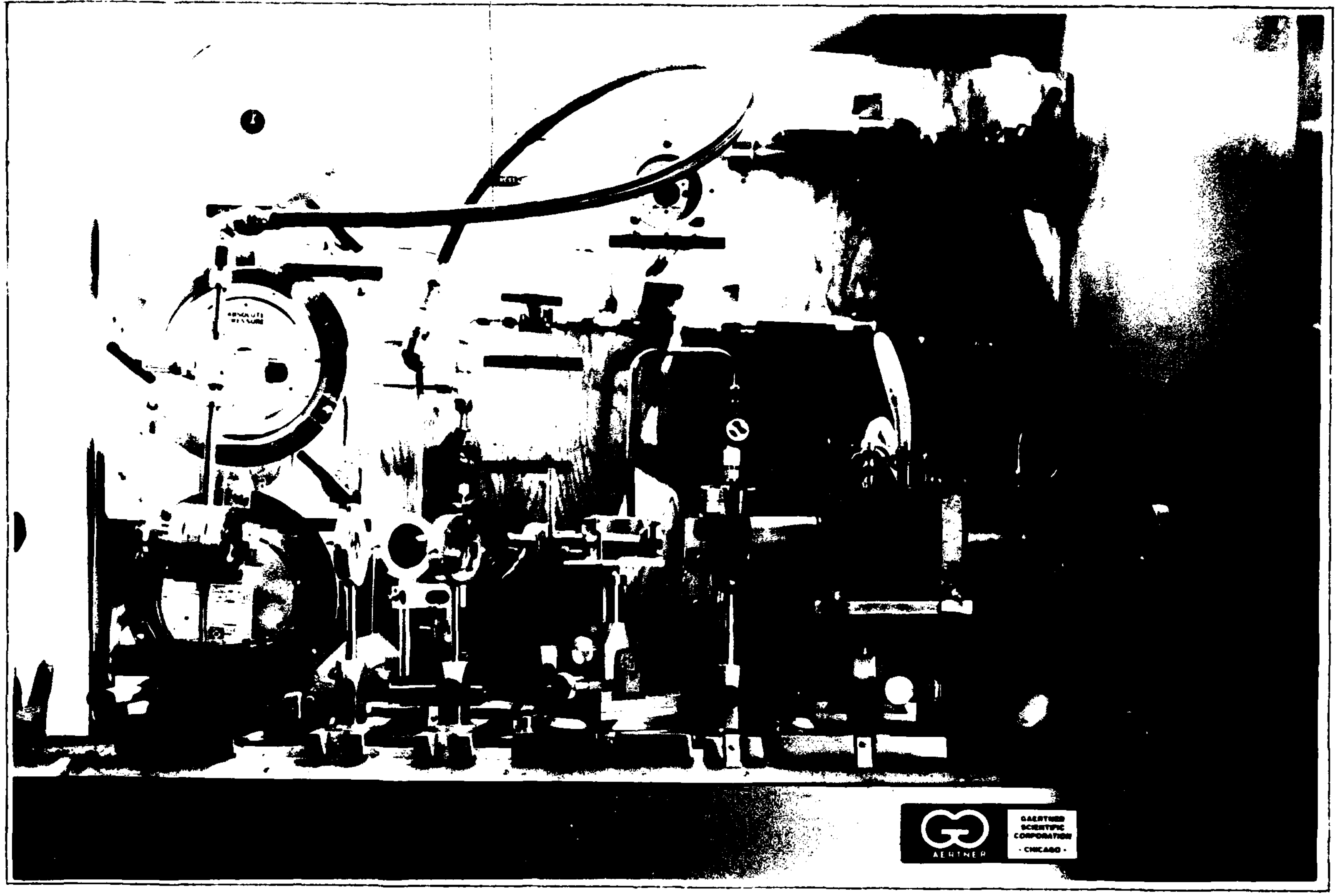


Figure 9. Photograph of Laser Photodeposition Set-up

phase-matching with an ADP frequency doubling crystal discussed below. After the laser beam entered the fume hood it was transmitted through a 2 inch diameter quartz lens having a 12 inch focal length. This lens focused the 5145Å radiation into a frequency doubler ADP crystal ($NH_4H_2PO_4$) which was cooled to -15°C and made by Quantum Technology Corp. The crystal was cooled with a commercial water cooler. The frequency doubler emitted both 5145Å radiation and 2572Å radiation. Both the visible and ultraviolet radiation was then incident on an ultraviolet transmitting visible absorbing filter having a transmission profile shown in Figure 10. The emitted radiation was then incident on a 60° quartz prism to separate the coincident 5145Å and 2572Å beams. The prism was still required since the filter did not completely eliminate the 5145Å laser radiation. The prism separated the 5145Å radiation from the 2572Å with an approximate angle of separation of 7°. The 5145Å was then eliminated by an iris. Since radiation at 2572Å is not visible to the human eye, an aid had to be used so that its path could be detected. So, an u-v luminescent powder was bonded to a 3 by 5 inch card with Vacseal, a standard adhesive high vacuum leak sealant. The 2572Å radiation caused the powder to fluoresce and the beam's path was detected. The ultraviolet radiation was then reflected off of two aluminum coated mirrors into the test

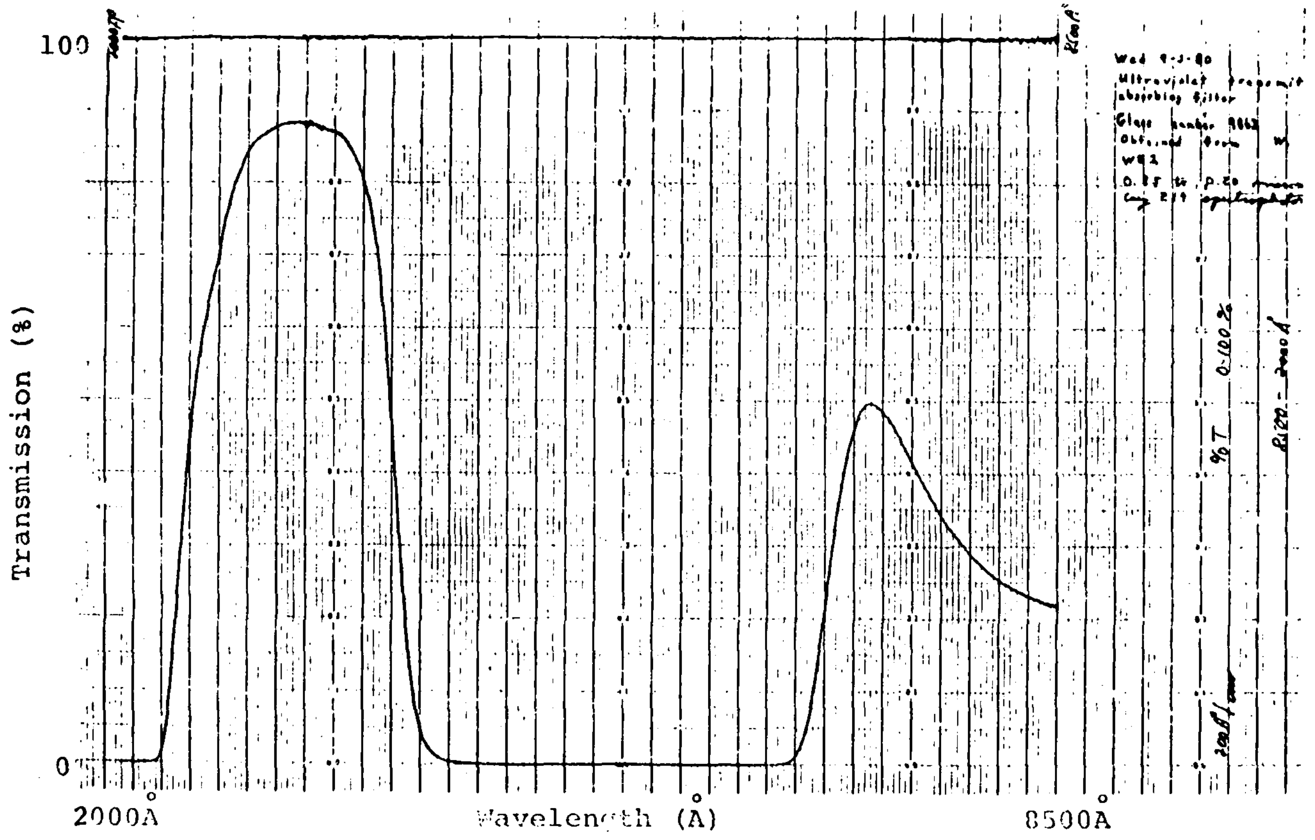


Figure 10. Transmission Profile of Ultra-Violet Filter

cell. Aluminum coatings have a high reflectivity at 2572Å of 92.2% (Ref 33:6-157). Prior to entering the test cell, the 2572Å radiation was then focused by a lens with a two inch focal length. The len's focal point was positioned a few millimeters in front of the back surface of the test cell's quartz substrate. Focusing of the 2572Å radiation was done to increase the dissociation rate of the organometallic molecules (see Equation 1). After propagating through the test cell, the 2572Å radiation was detected by a RCA model 8185 photomultiplier that was connected to a lock in amplifier which had an output recorded by a strip chart recorder.

(C) Incoherent Light Photodeposition Set-Up/Procedure

During the laser deposition experiments, no depositions were observed with the 2572Å laser light. Measurements of the absorption curves (see Section IV-B) illustrated that wavelengths lower than 2420Å were required to photodissociate the Zn- and Se- dimethyls in a single step photon process. Since the laboratory had no operating laser at such a low wavelength, an incoherent Oriel Mercury arc lamp (model HR-1) with a 1000 watt u-v output centered at 2537Å was used. This source emitted down to 2100Å. Figure 11 shows the output spectra from the Hg arc lamp source (Ref 34). Integrating under this light source indicates that less than 1% or only

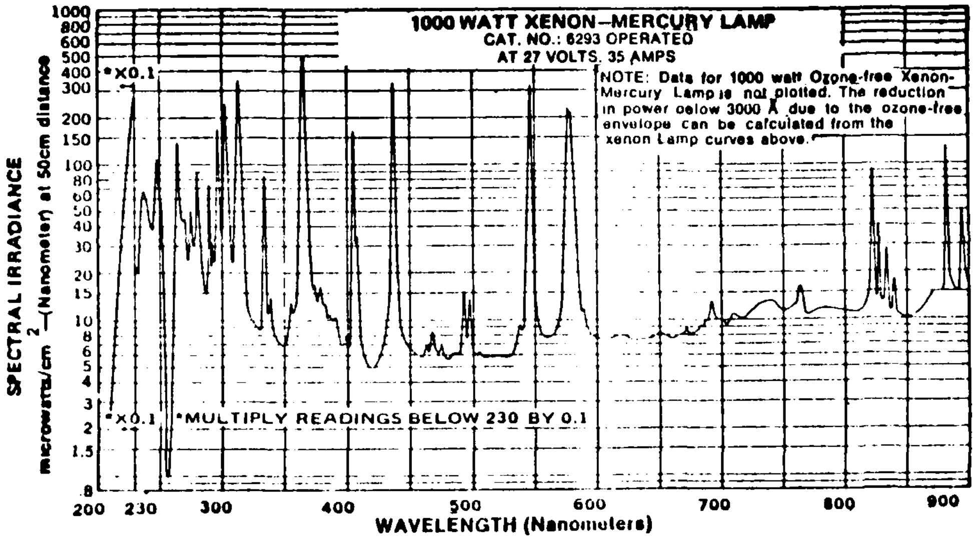


Figure 11. Output Spectra of 1000 Watt Hg Arc Lamp

10 watts of u-v light is existant below 2420Å, the threshold for a single step photon dissociation of either $Zn(CH_3)_2$ or $Se(CH_3)_2$. Since this source was not monochromatic, no optimum ratio of the Zn and Se organometallics could be determined to produce a stoichiometric formation of ZnSe. However, this lamp source did deposit Zn, Se, and ZnSe films.

In Figure 12, a schematic of the incoherent deposition experiment is shown. Figure 13 is an actual photograph of the experiment. This arrangement was very simple in that it consisted of only the Hg arc light source, two lenses and the same test cell previously described. Because of the low u-v power available below 2420Å, the deposition rates were slow, having typical operational times of 1 to 4 hours. During the experimental test, the thin films could be seen growing in thickness on the quartz and/or sapphire substrates.

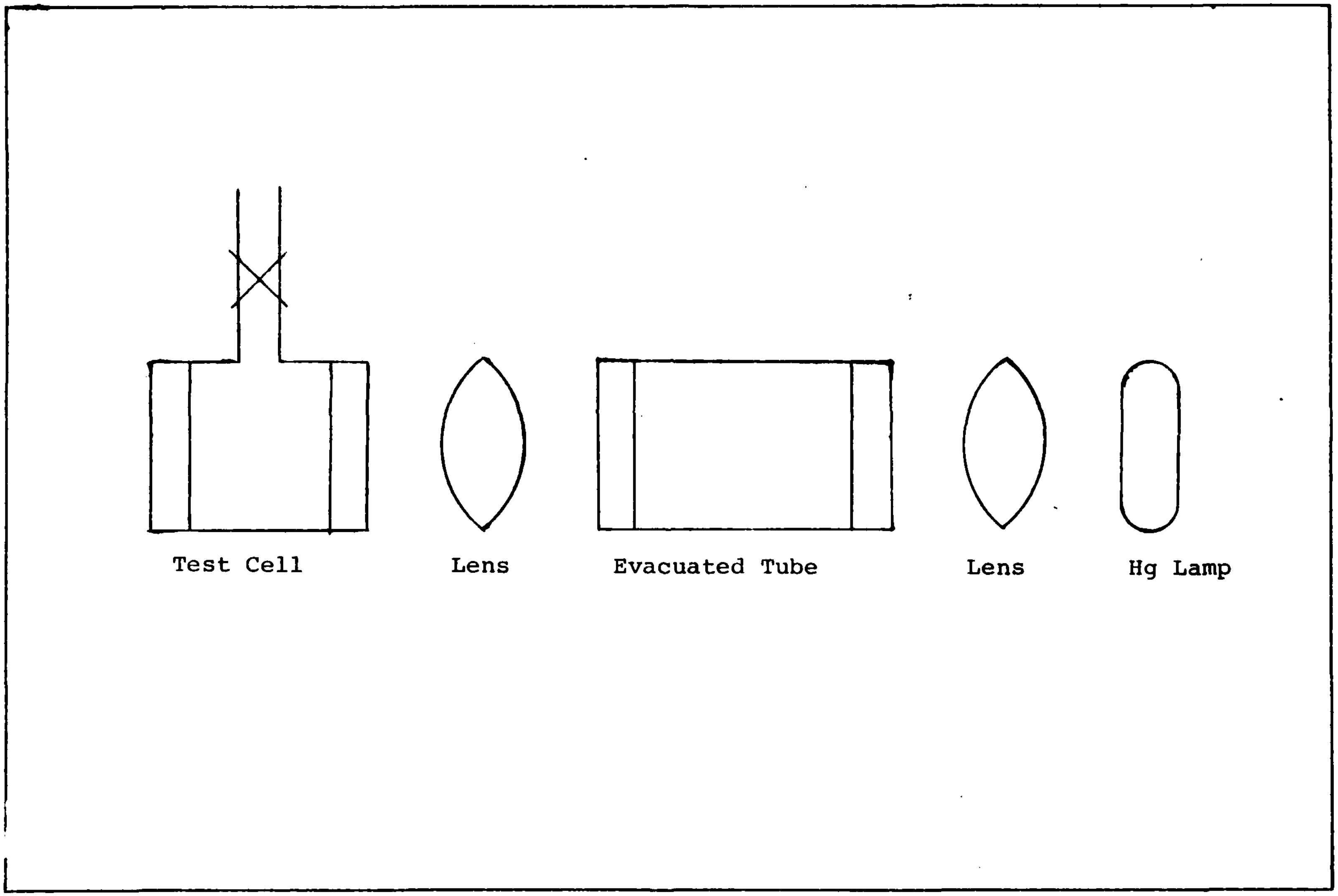


Figure 12. Incoherent Light Deposition Experimental Set-up

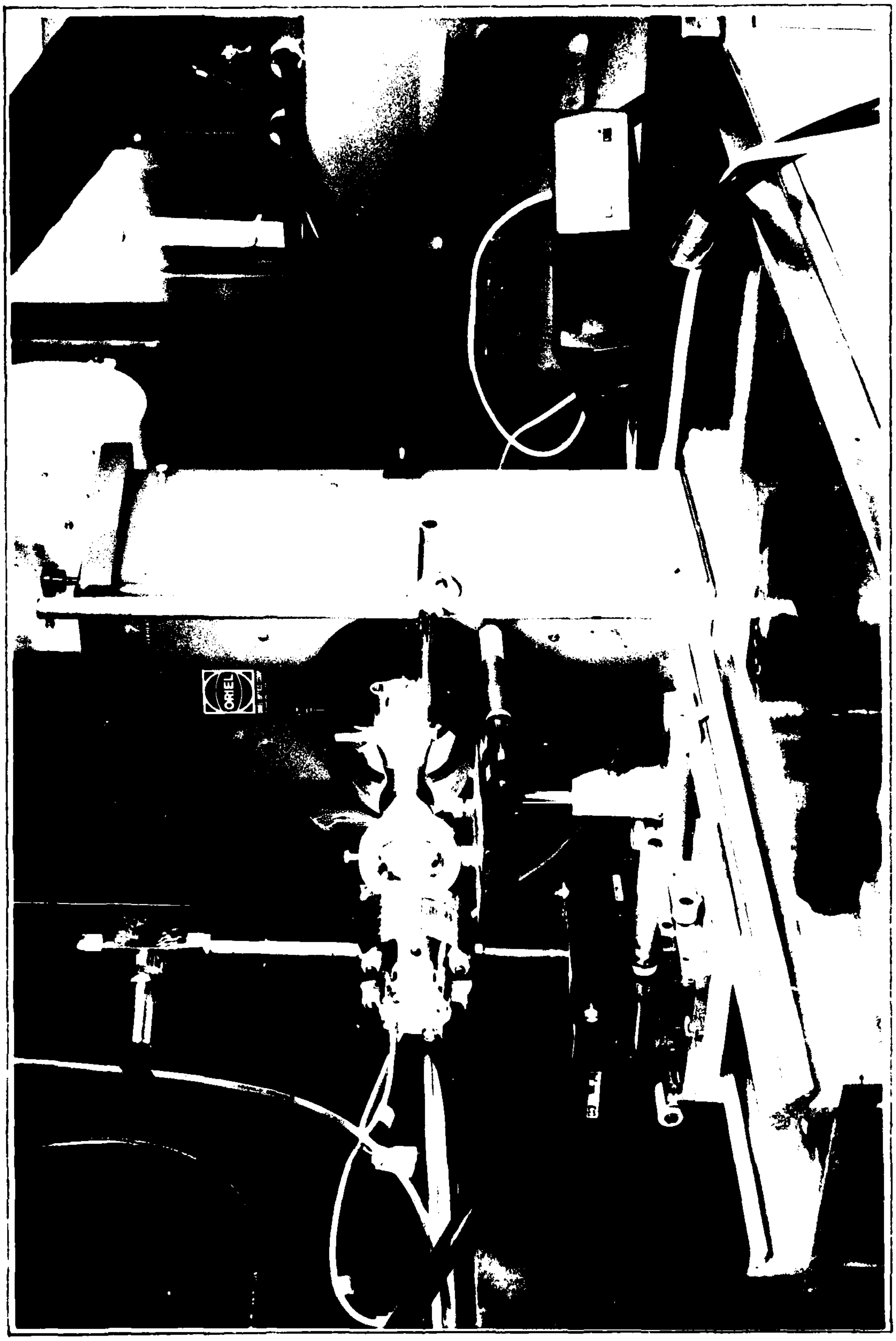


Figure 13. Photograph of Incoherent Light Deposition Set-up

IV Results and Discussion

When the frequency doubled Ar^+ laser radiation at 2572Å from the ADP crystal was propagated through the test cell, no thin film was deposited under any experimental conditions or for any mixtures of $Zn(CH_3)_2$ and $Se(CH_3)_2$ or Ar. All attempts were made to optimize the conditions for deposition. Some of these included focusing the beam, operating at high organometallic vapor pressures ($\sim$ 50 torr), and maximizing the power of the 2572Å radiation. However, none of these improvements resulted in a thin film deposition by photodissociation of the Zn- and Se- dimethyl molecules via the 2572Å photons. Such failure forced us to very carefully examine the dissociation cross section below 2600Å. Originally, Thompson stated that for $\lambda < 2600$Å, both Zn- and S- dimethyl are photodissociated in a single step photon process (Ref 17). However, in Section IV-B, absorption measurements in $Zn(CH_3)_2$ and $Se(CH_3)_2$ indicate that the threshold wavelength for dissociation is 2420Å not 2600Å. Thus, these results clearly indicate that the frequency doubled laser output at 2572Å would not photodissociate the dimethyls of Zn and Se as originally thought. Consequently, as an alternative, an incoherent Hg arc lamp source capable of emitting at wavelengths down to 2100Å was used. With this light source, thin films having large areas (> 1.5 cm diameter areas) with thickness up to 6000Å of Zn, Se and ZnSe were deposited on both quartz and sapphire substrates. In the following information presented, all of the depositions were produced using the incoherent Hg arc lamp source.

(A) Thin Film Depositions

Qualitatively, the thin films of Zn, Se, and ZnSe had distinct features. The Zn films were characterized by a grey color (Ref 35:B-146) while the Se had a hazy appearance. The thin films deposited from a gas mixture of $Zn(CH_3)_2$ and $Se(CH_3)_2$ had the characteristics of both the pure Zn and Se plus a yellow color typically observed in the ZnSe thin films (Ref 36). The combined characteristics of the ZnSe films is thought to be due to the experimental inability to produce by photodissociation free Zn and Se stoichiometrically. Such an effect should be eliminated by the use of a laser. Using a combination of lasers should enable the dissociation rate R_d to be the same for both the Zn- and Se- dimethyls. Once these two rates are made equal, the process for forming the ZnSe stoichiometrically can be determined and then optimized.

In Figure 14, a photograph of two typical thin films is shown. The deposit on the right shows an unmasked u-v light source deposition. All of the deposited thin films of Zn, Se, and ZnSe had features similar to this deposit. The only difference was their color and thickness. Under an electron microscope, definite differences in their structure were observed. This is discussed below. The deposit on the left in Figure 14 is a deposition produced by masking the u-v light source. The deposited film was a direct replica of the masked u-v light source beam. The substrate on edge illustrates the typical thickness of the substrates used.

When a BK-7 piece of glass, which does not transmit radiation below 3400Å, was inserted between the Hg arc lamp source and the test cell, no deposition was ever detected for run times as long as two hours. During the depositions, a thermocouple was used to determine if the substrate was being heated substantially. For all depositions, the substrate had a maximum rise in temperature of only 5°C. Considering that the well depth for these two organometallics is 60 Kcal (see Figure 1), no pyrolysis of these molecules could of occurred. These two physical facts, definitely indicate that both $Zn(CH_3)_2$ and $Se(CH_3)_2$ are dissociated by the u-v photons. No other process could produce this result.

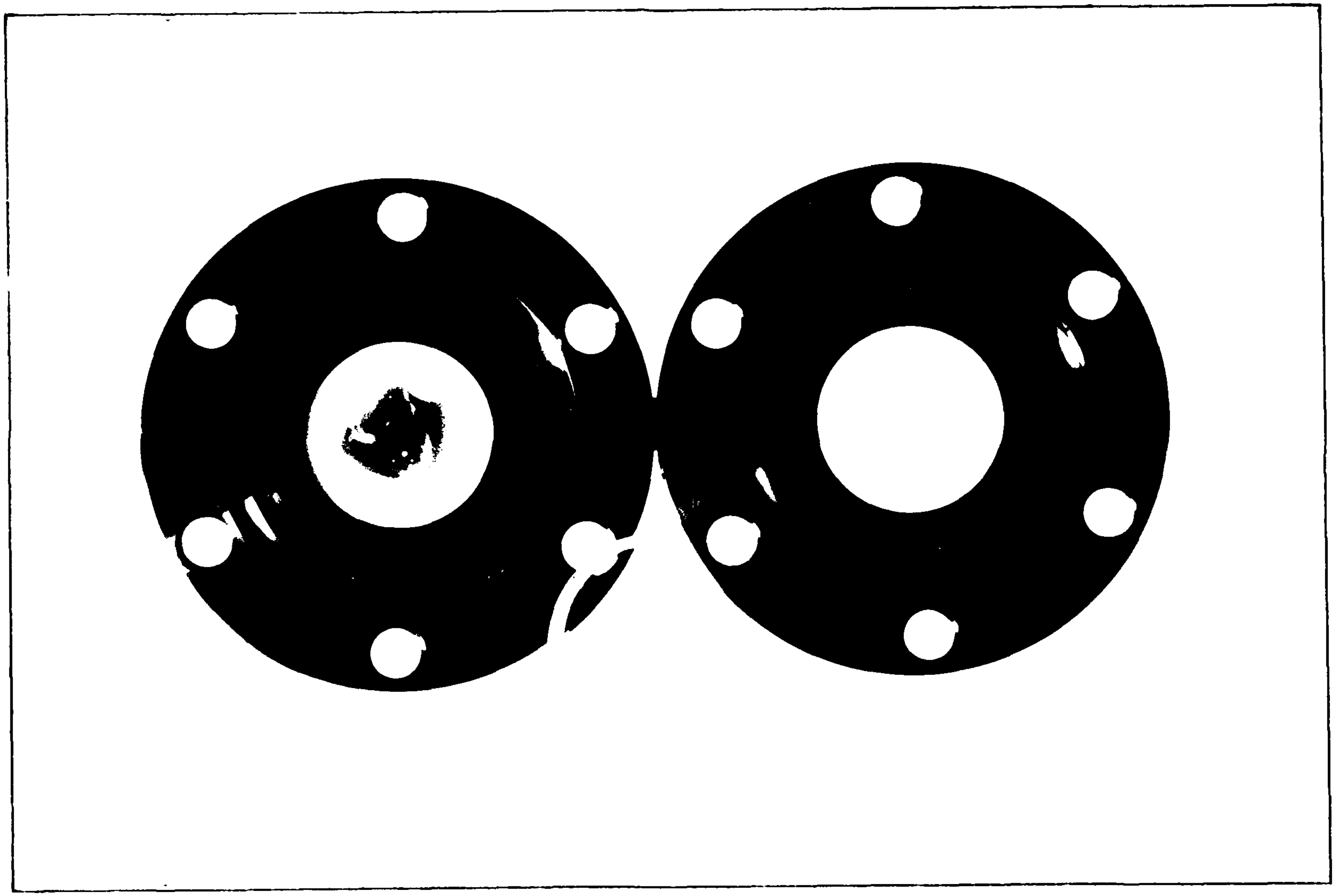


Figure 14. Photograph of Typical Thin Films Via Photodeposition

Once these depositions were made, specific diagnostic tests were performed. First, a Hitachi scanning electron microscope Model S 500 was used to analyze the elemental content of these films. Figures 15-17 show typical results. In the top of each figure are the x-ray emissions for the elements and in the bottom of each figure the superimposed K and L line spectra (Ref 37 and 38). For all of the figures, only the characteristic elements Zn and Se are present except for the Cl atoms in the Zn depositions.

The appearance of atomic Cl was somewhat surprising until it was realized that chlorine is used in the preparation of $Zn(CH_3)_2$ (Ref 32). Upon the observation of this impurity in the film, the mixture of $Zn(CH_3)_2$ and argon was analyzed with a mass spectrometer to determine the impurities in the gas sample. Unfortunately, no Cl_2 or any chloride molecules could be detected within the sensitivity of the mass spectrometer, approximately 5 ppm. Some chlorine atoms are still expected to be present in the gas since it was manufactured using chlorine (Ref 32). With laser dissociation, an impurity should be eliminated since it would have a different wavelength region for dissociation than either the $Zn(CH_3)_2$ or $Se(CH_3)_2$. For example, the absorption curve of Cl_2 shown in Figure 18 illustrates that radiation around 3300Å is required to

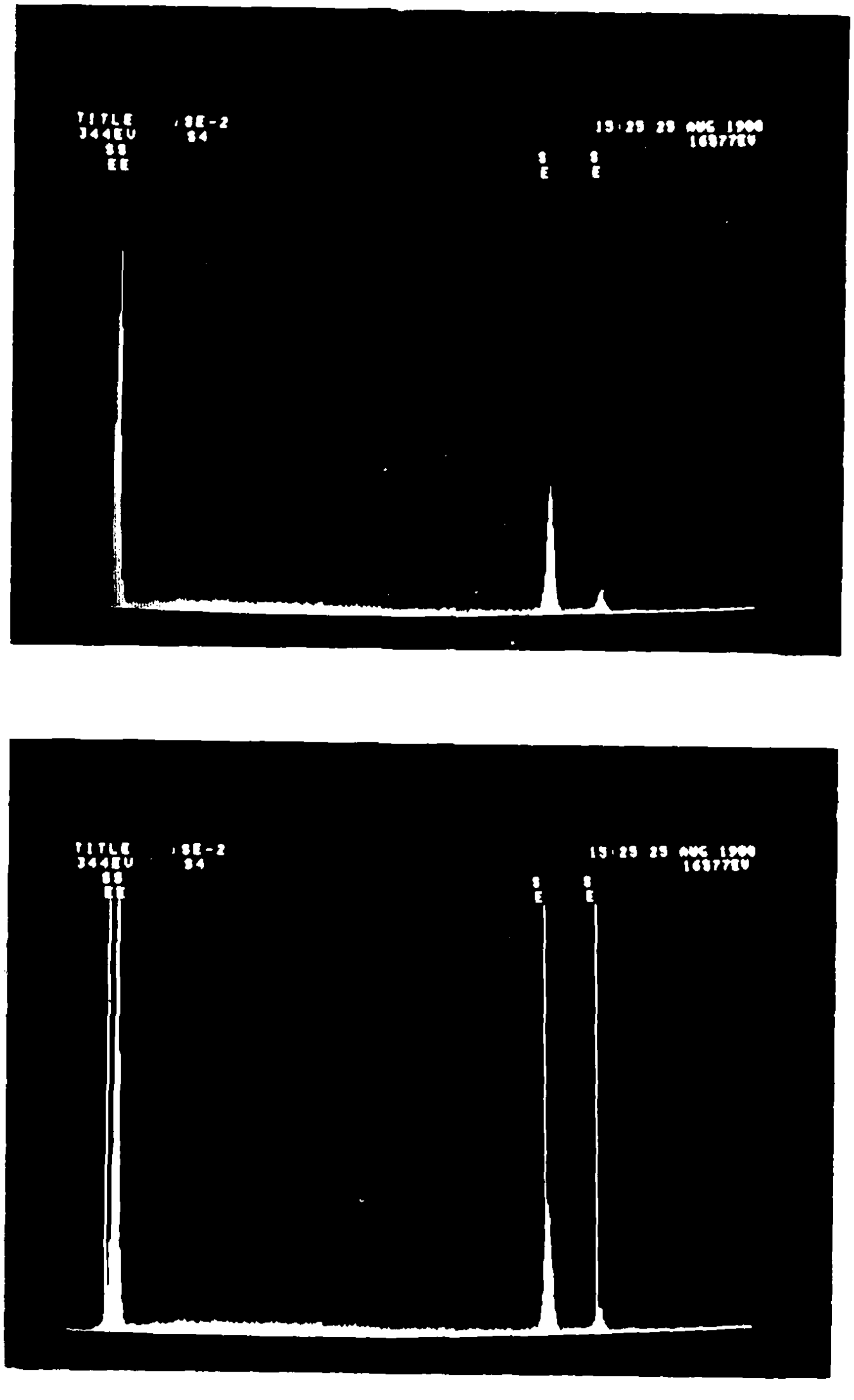


Figure 15. Scanning Electron Microscope Analysis of a Selenium Thin Film

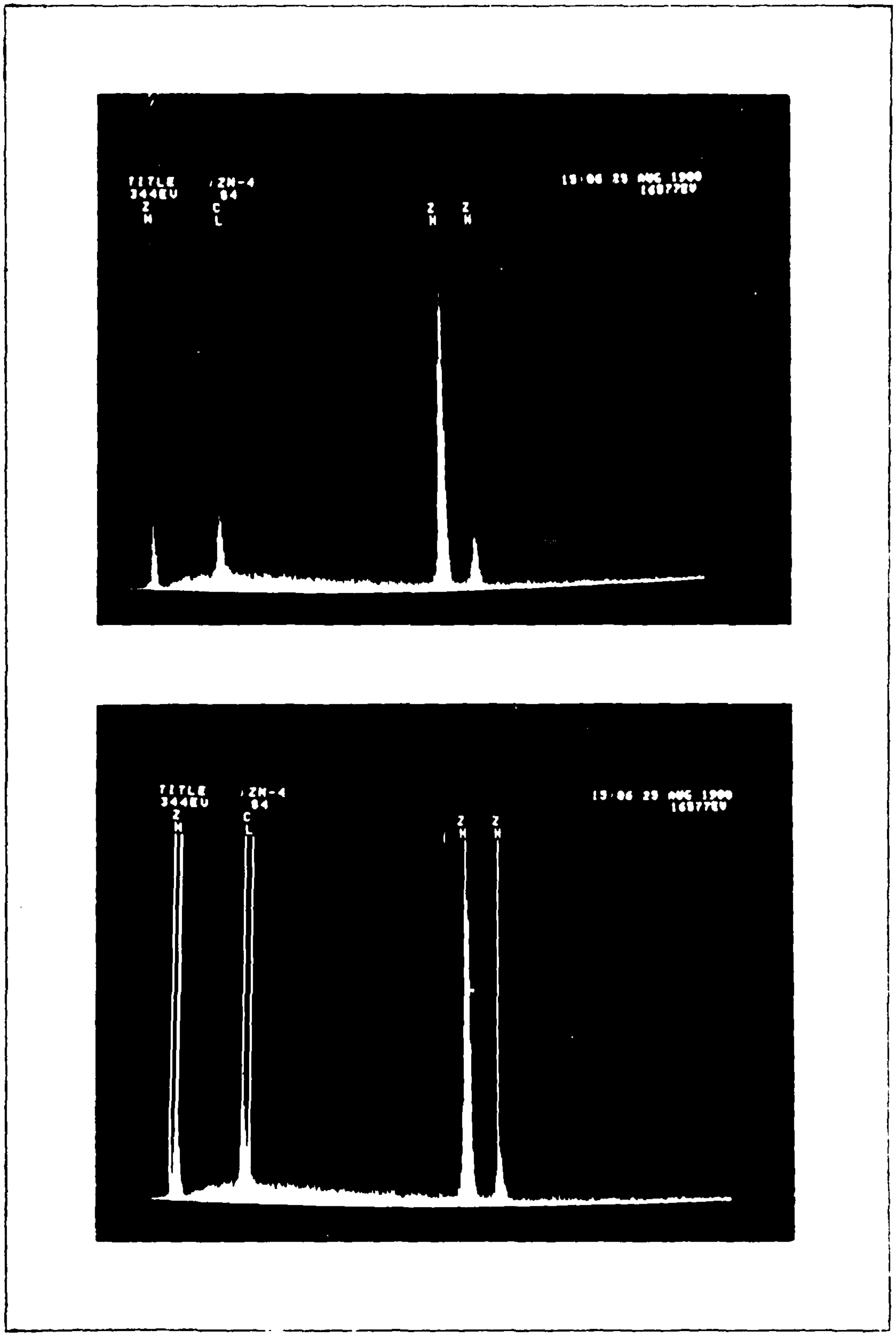


Figure 16. Scanning Electron Microscope Analysis of a Zinc Thin Film

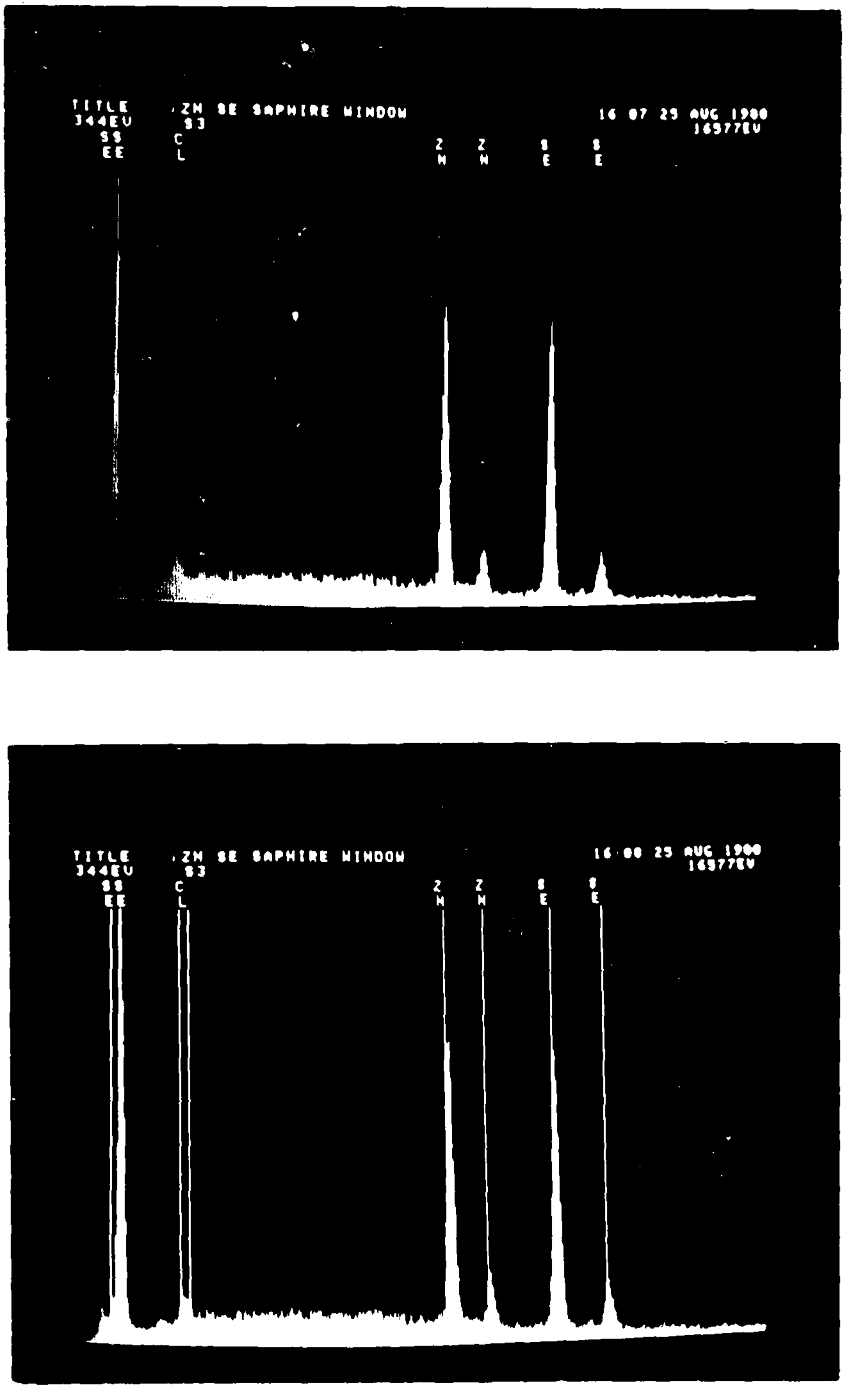


Figure 17. Scanning Electron Microscope Analysis of a Zinc Selenide Film

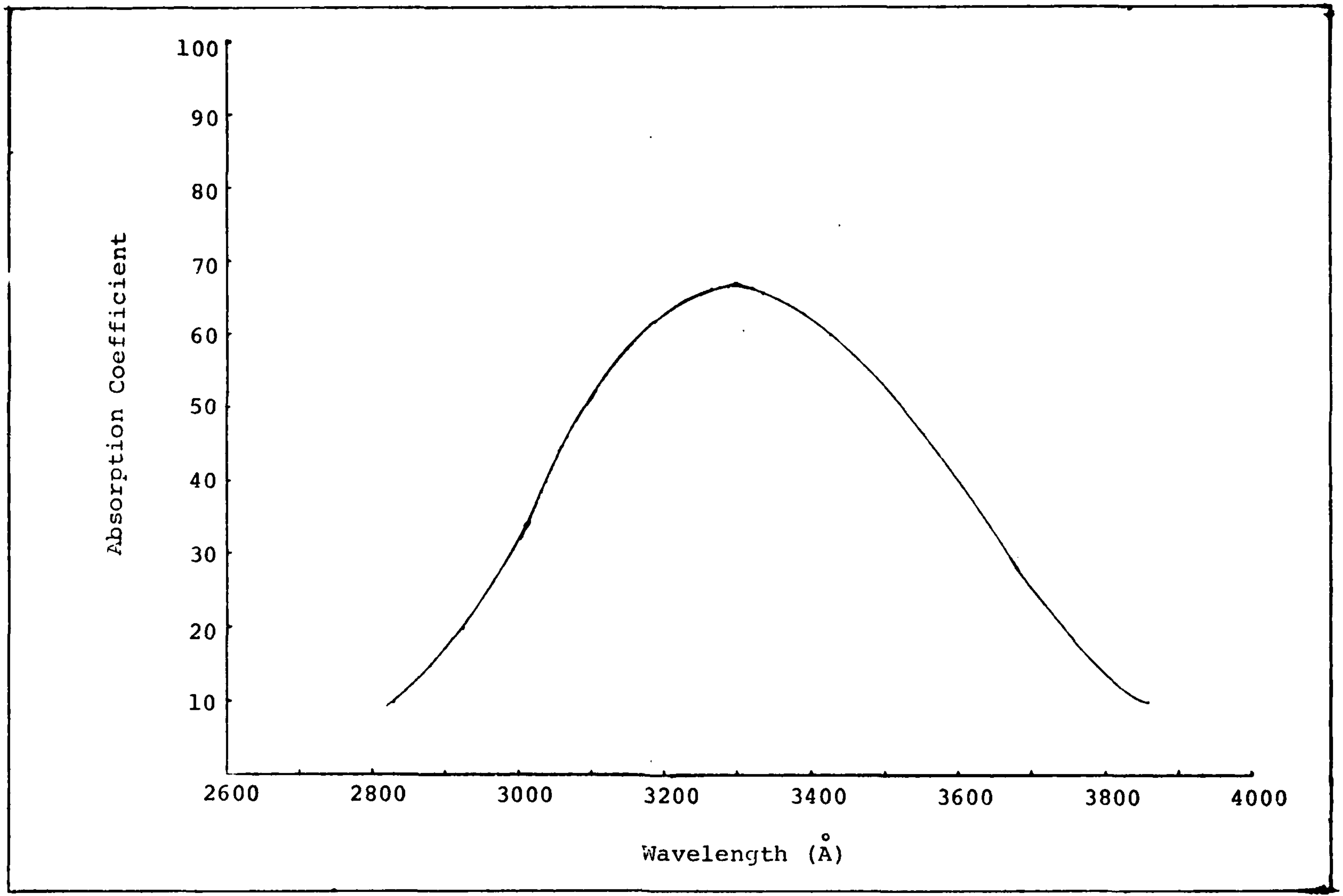


Figure 18. Absorption Curve of Cl_2

dissociate free Cl atoms. In addition, there are techniques to produce $Zn(CH_3)_2$ without using chlorine (Ref 39).

Another important issue dealing with these thin films is the question as to whether there exist any C or H atoms trapped in the thin film, since these atoms are present in gaseous organometallic molecules. Unfortunately, neither one of these elements can be detected with any of the diagnostical equipment existing at AFWL. Consequently, the content of C and H impurities in these films is unknown at this time. Future diagnostic tests should be able to detect any C impurities. The extent of H in the films is extremely difficult to determine. Only Rutherford scattering techniques can be used (Ref 40). If such impurities are found, certain scavengers, like cyclohexane (Ref 41) for the liberated CH_3 radical, may be used to eliminate their trapping in the thin film.

The next diagnostic test performed was to examine the microstructure of the thin films with the previously used scanning electron microscope. All photographs of the film's microstructures (Figs 19-21) contain a 5μ line on their right hand side, except for the top photo in Fig 21, which has a 50μ line. The magnification of the photos was 2000x except the top photo in Fig 21 which was taken at 500x. Notice that the Zn film (top photograph of Figure 19) is

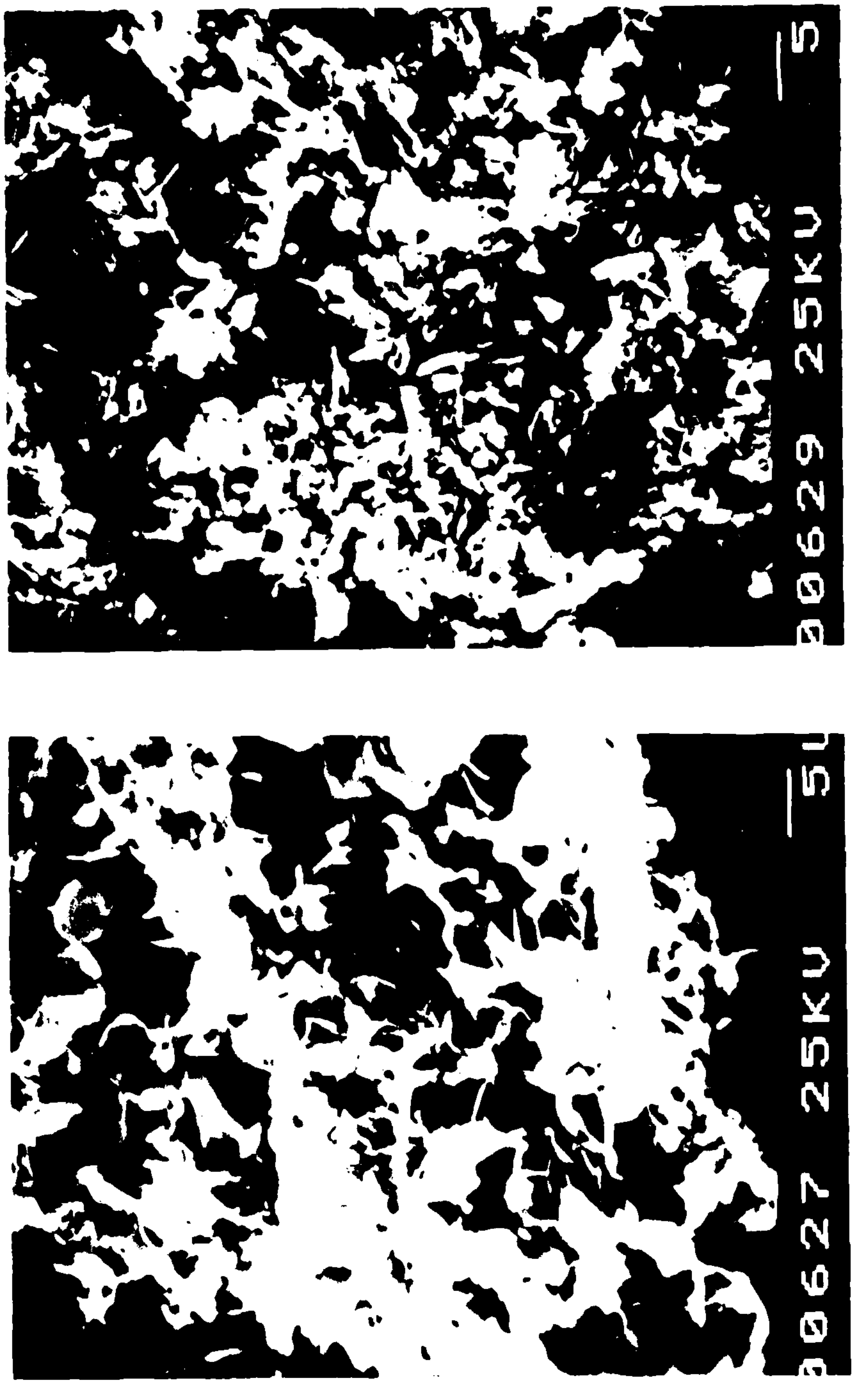


Figure 19. Scanning Electron Microscope Photograph of Zinc Film's Microstructure at 2000x Magnification

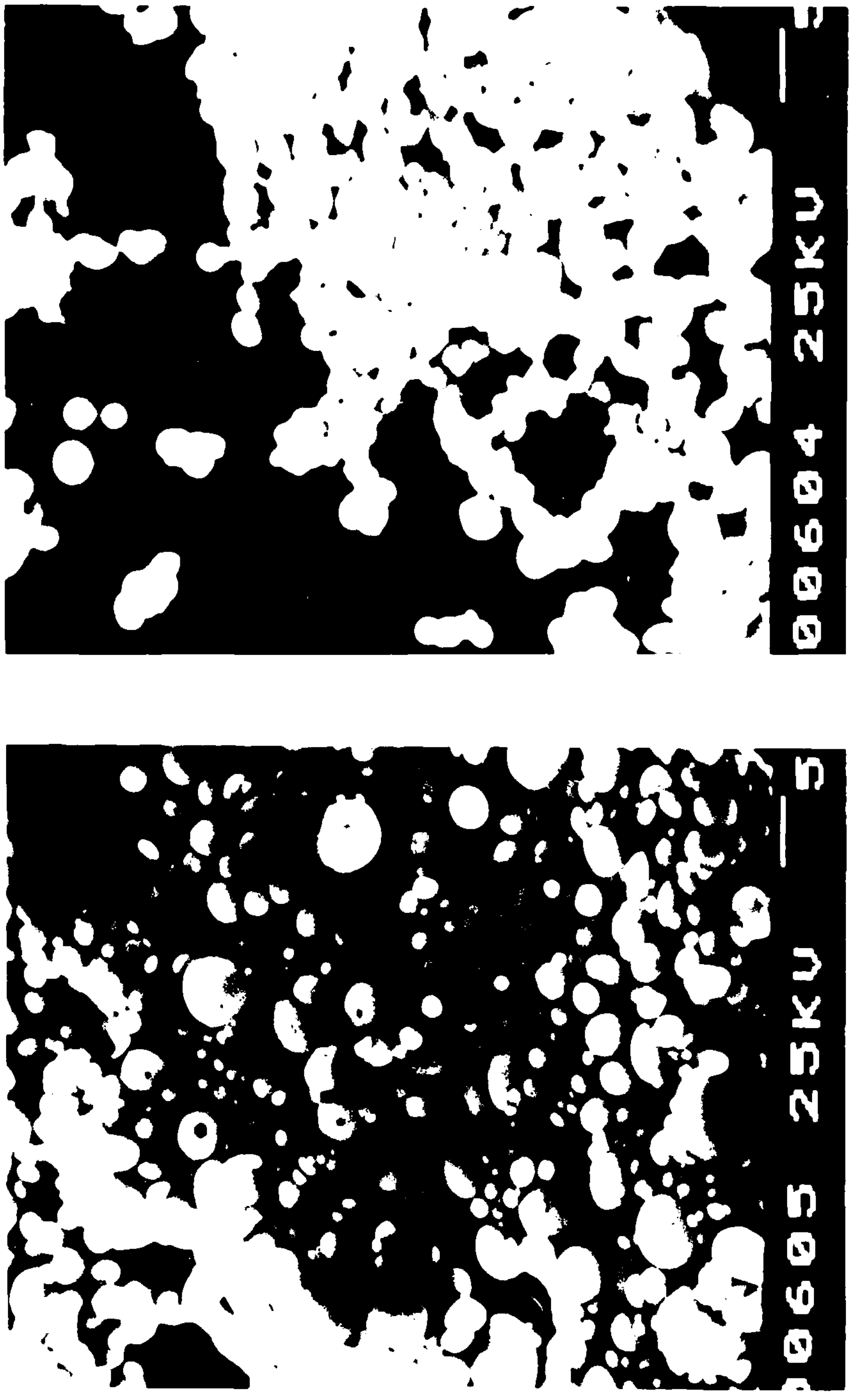


Figure 20. Scanning Electron Microscope Photograph of Selenium Film's Microstructure at 2000x Magnification

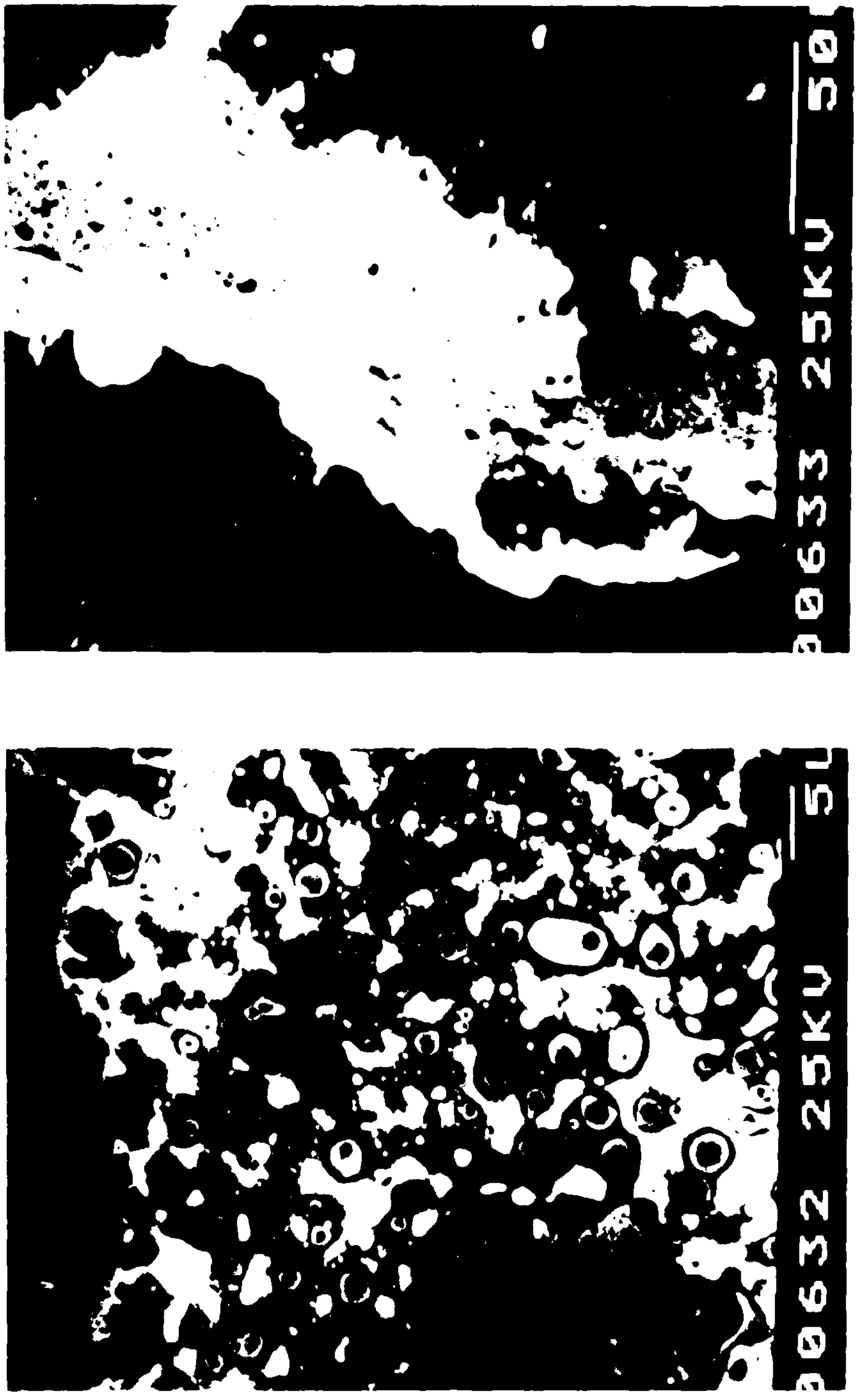


Figure 21. Scanning Electron Microscope Photograph of Zinc-Selenide Film's Microstructure at 2000x Magnification

flaky in structure while the Se film (Figure 20) has a ball-like structure. After the zinc film oxidized its microstructure changed to a rosette microstructure (bottom photograph of Figure 19). The ZnSe film (Figure 21) has a combination of both structures.

To determine the film thicknesses, a standard stylus depth thickness measuring system, Rank Scherr Tumico's talystep, was used. Some difficulty was experienced in determining the Zn thickness, since highly pure Zn is very soft. A typical scan of the film's surface and thickness is given in Figure 22. The thickness of this film is 6000Å and has a uniformity of 6%. It is believed that a much better uniformity could be achieved if the light source's uniformity could be improved using an optical integrator and if a very flat surfaced substrate was used.

The results presented here are very promising. Naturally, future work needs to be done using coherent laser sources to control the stoichiometric depositions of thin films of ZnSe. The use of such sources should produce very good ZnSe films.

(B) Zn- and Se- $(CH_3)_2$ Ground State Absorption

As previously stated, the laser deposition experiment using the ADP frequency doubled output at 2572Å failed to produce a thin film deposition of Zn or Se when either

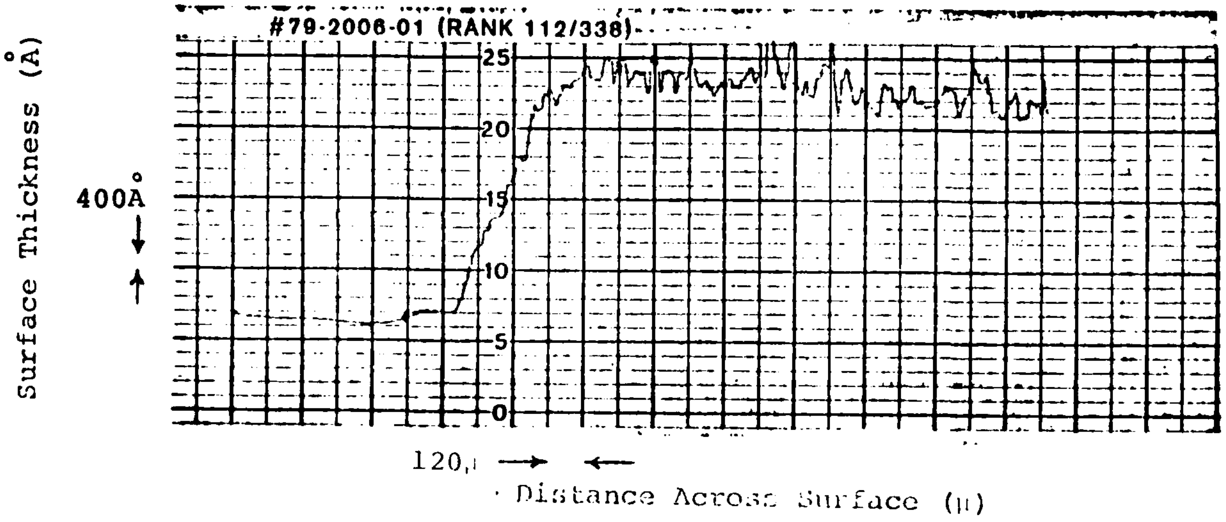
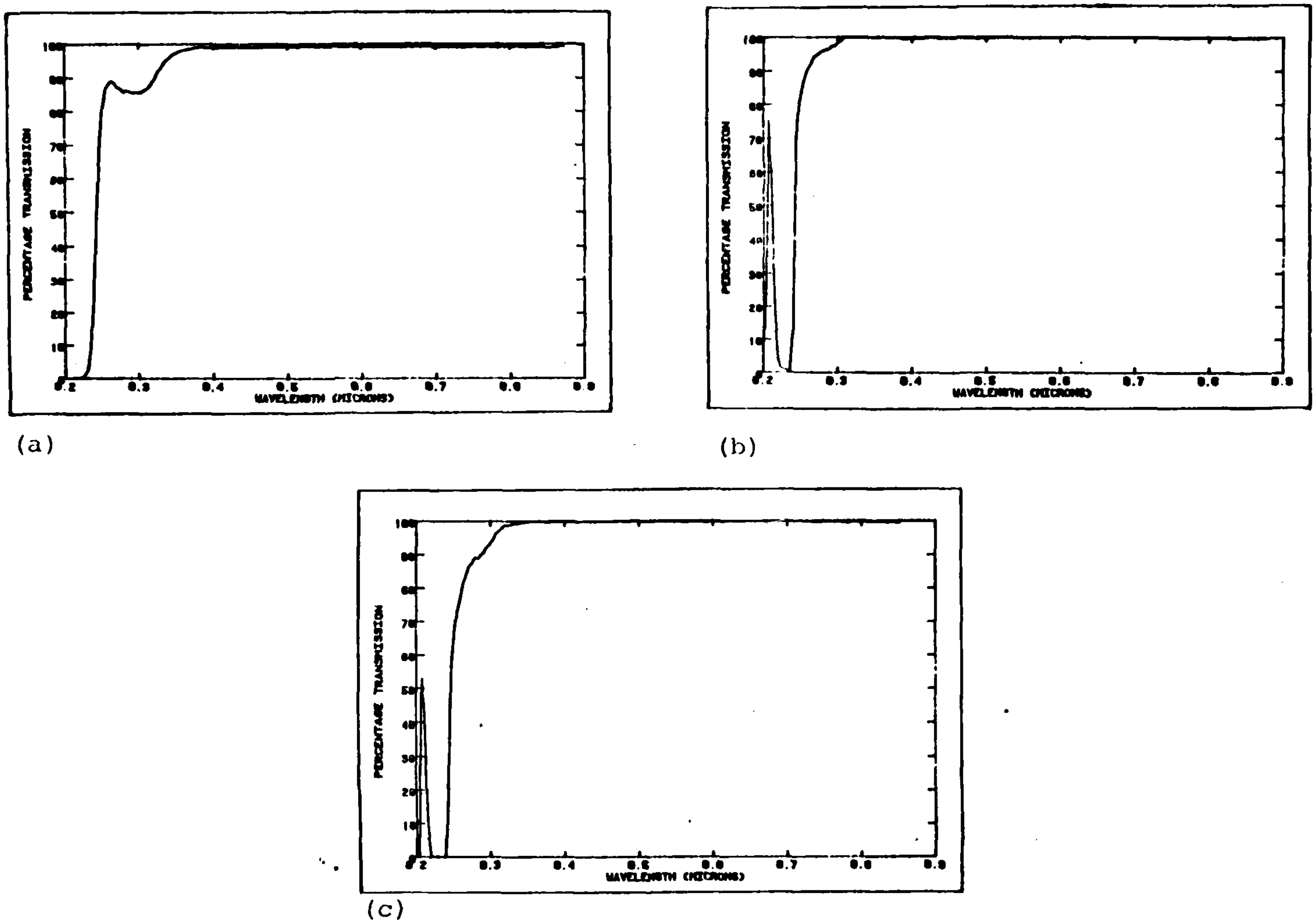


Figure 22. Stylus Scan of a Typical Zinc Film's Surface and Thickness

$Zn(CH_3)_2$ or $Se(CH_3)_2$ was used. This was quite surprising based on the absorption data reported by Thompson (Ref 17). He reported that the threshold wavelength for the photodissociation of $Zn(CH_3)_2$ was 2600Å. No data was available for $Se(CH_3)_2$. To resolve this discrepancy, very exact transmission measurements through the gaseous $Zn(CH_3)_2$ and $Se(CH_3)_2$ organometallics were made using a Cary spectrometer. The results are presented in Figures 23-24. Starting at approximately 3500Å, there is a gradual decrease in the transmission with decreasing wavelength until an abrupt change at 2420Å. This type of transmission behavior can be explained by realizing that both of the organometallic molecules are physically very large and that Rayleigh scattering varies as $1/\lambda^4$ (Ref 42:652). Combining these two effects strongly indicates that these molecules scatter the radiation, giving an inaccurate assessment of the dissociation threshold. At 2400Å, there exists a very sharp cut-off in the transmitted signal. Consequently, it is believed from the measurements that the correct threshold is 2420Å not 2600Å as previously reported.

Using the data shown in Figures 23-24, a magnitude for the absorption cross section for the photodissociation was calculated, which is shown in Figure 25 for both Zn- and Se- dimethyl. The maximum value for these u-v dissociating

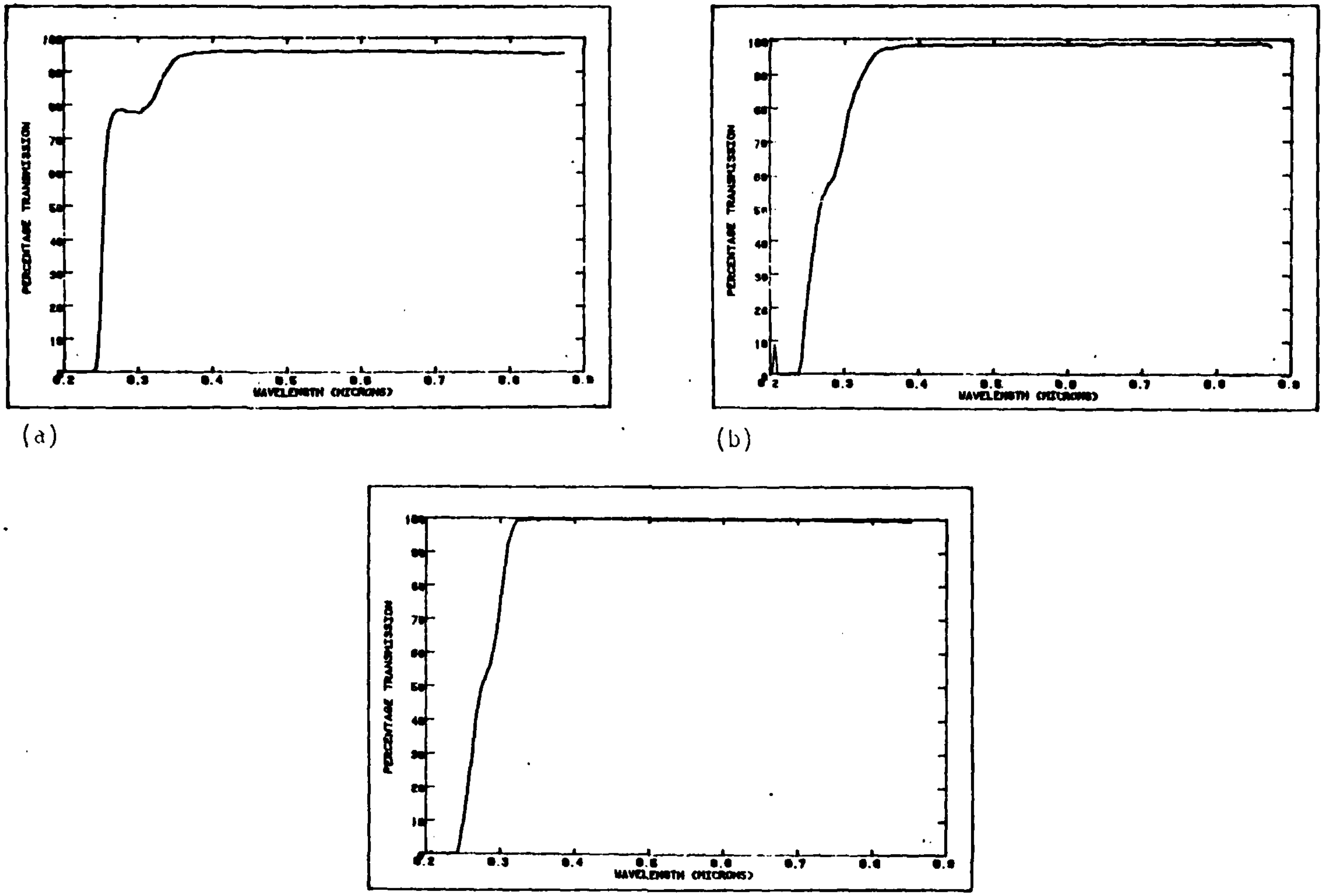


(a)

(b)

(c)

Figure 23. Transmission Spectra From 0.2 to 0.875 Microns of 10 Torr (3.22×10^{17} molecules/cm^3): (a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$ (c) Both $Zn(CH_3)_2$ and $Se(CH_3)_2$



(a)

(b)

(c)

Figure 24. Transmission Spectra From 0.2 to 0.375 Microns of 12 psi Ar Mixed With 10 Torr (3.22×10^{17} molecules/cm^3): (a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$ (c) Both $Zn(CH_3)_2$ and $Se(CH_3)_2$

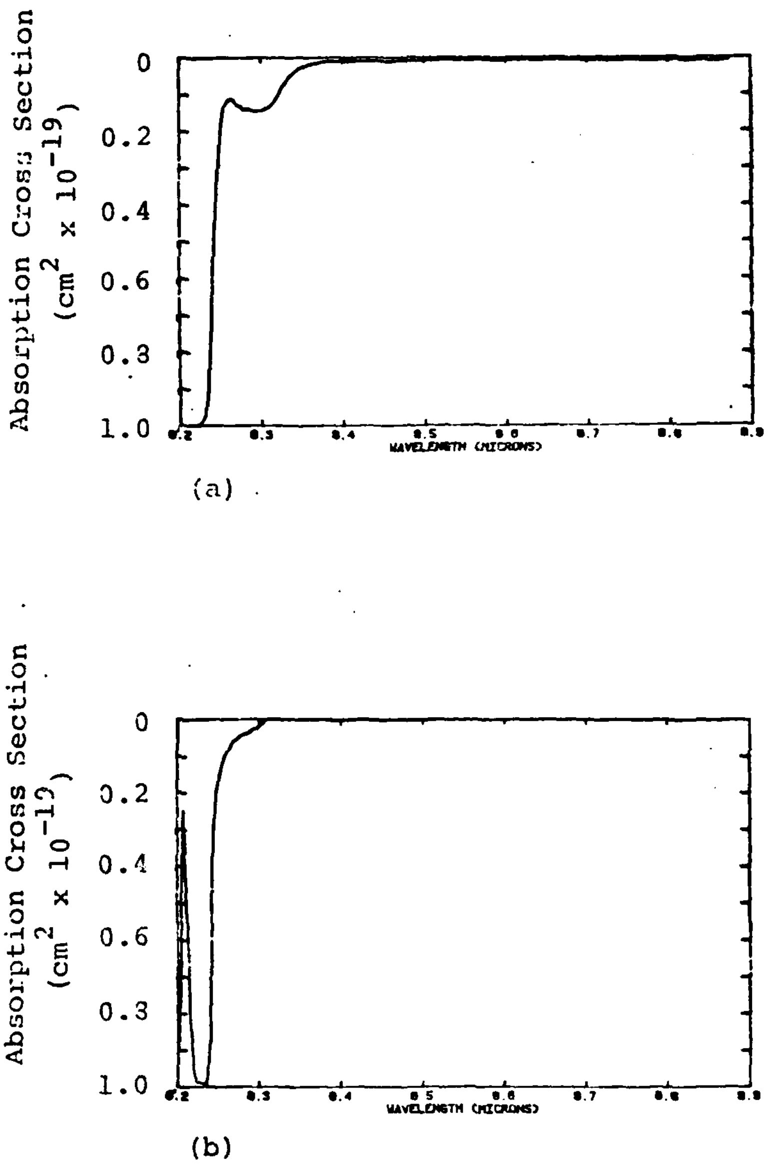


Figure 25. u-v Absorption Cross Sections (a) $Zn(CH_3)_2$
(b) $Se(CH_3)_2$

cross sections is approximately 10^{-19} cm^2. Since one of the ultimate goals is to produce ultra high purity thin films in order to possibly increase the energy damage threshold for laser mirrors, it was decided to measure the absorption cross sections over the region from 0.2 to 20 microns. No absorption exists between .3 and 1.6 microns for either $Zn(CH_3)_2$ or $Se(CH_3)_2$. Figure 26-28 shows typical IR absorption data and in Figure 29, the corresponding absorption cross sections are depicted.

Several interesting and very important points can be deduced from these curves. First, there are some regions where both the Zn- and Se- dimethyl absorption overlap. The transition around 3.4μ is a good example. Such a common IR absorption indicates that it is due to a vibration in the CH_3 radicals. A different type of IR absorption can be accurately deduced as a vibrational effect due to the Zn or Se interaction with the CH_3 radical. Such is the case for the $Zn(CH_3)_2$ absorption between 5.6 and 5.9μ and the $Se(CH_3)_2$ absorption centered at 10.6μ. In addition there is the IR absorption of $Se(CH_3)_2$ at 1.65μ and between 2.2 and 2.4μ. An appropriate laser for these two bands would be respectively a CO and CO_2 laser, as the first leg in a two-step process. The second photon would be from a KrF laser at 2480Å. In Figure 30, the physical concept is

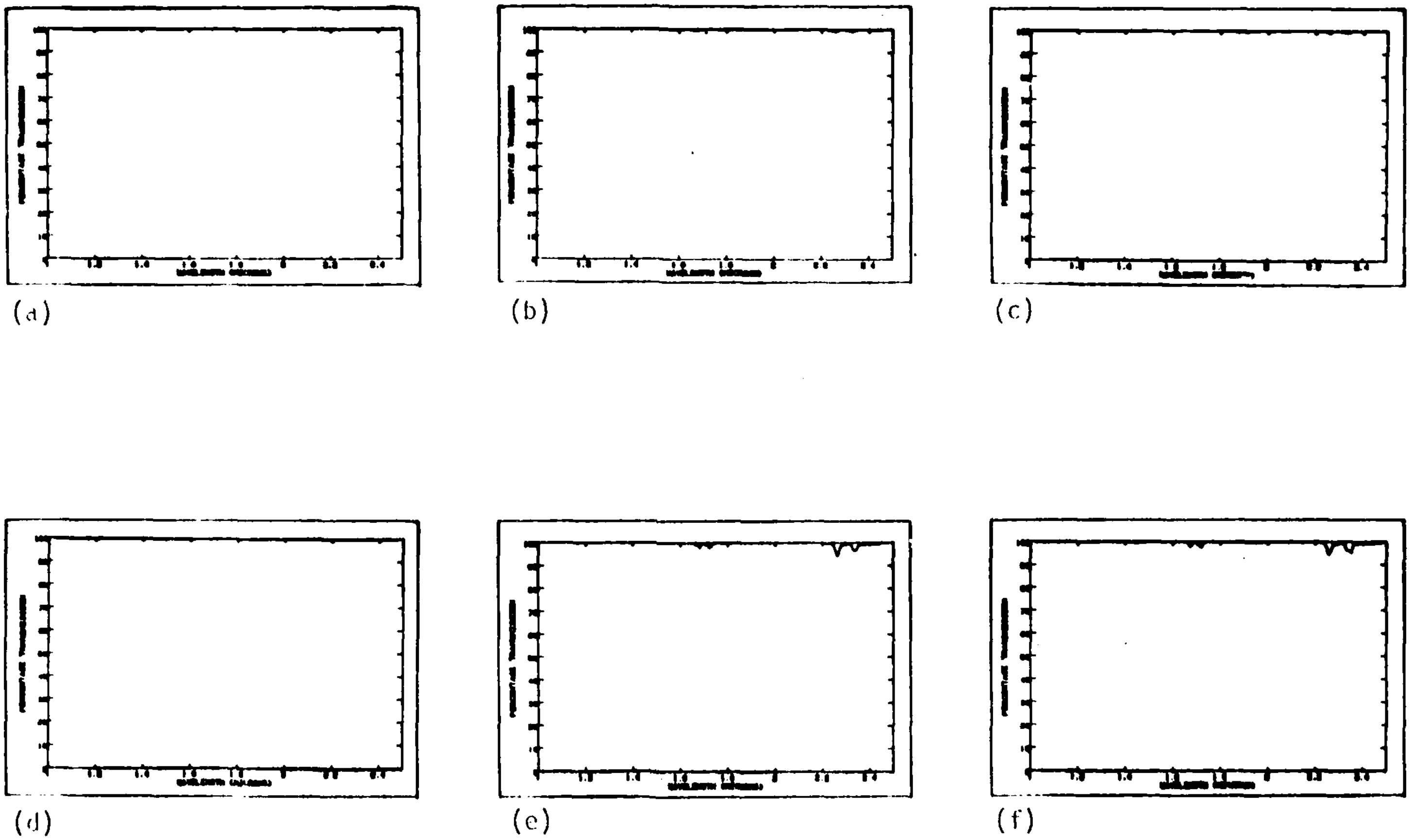
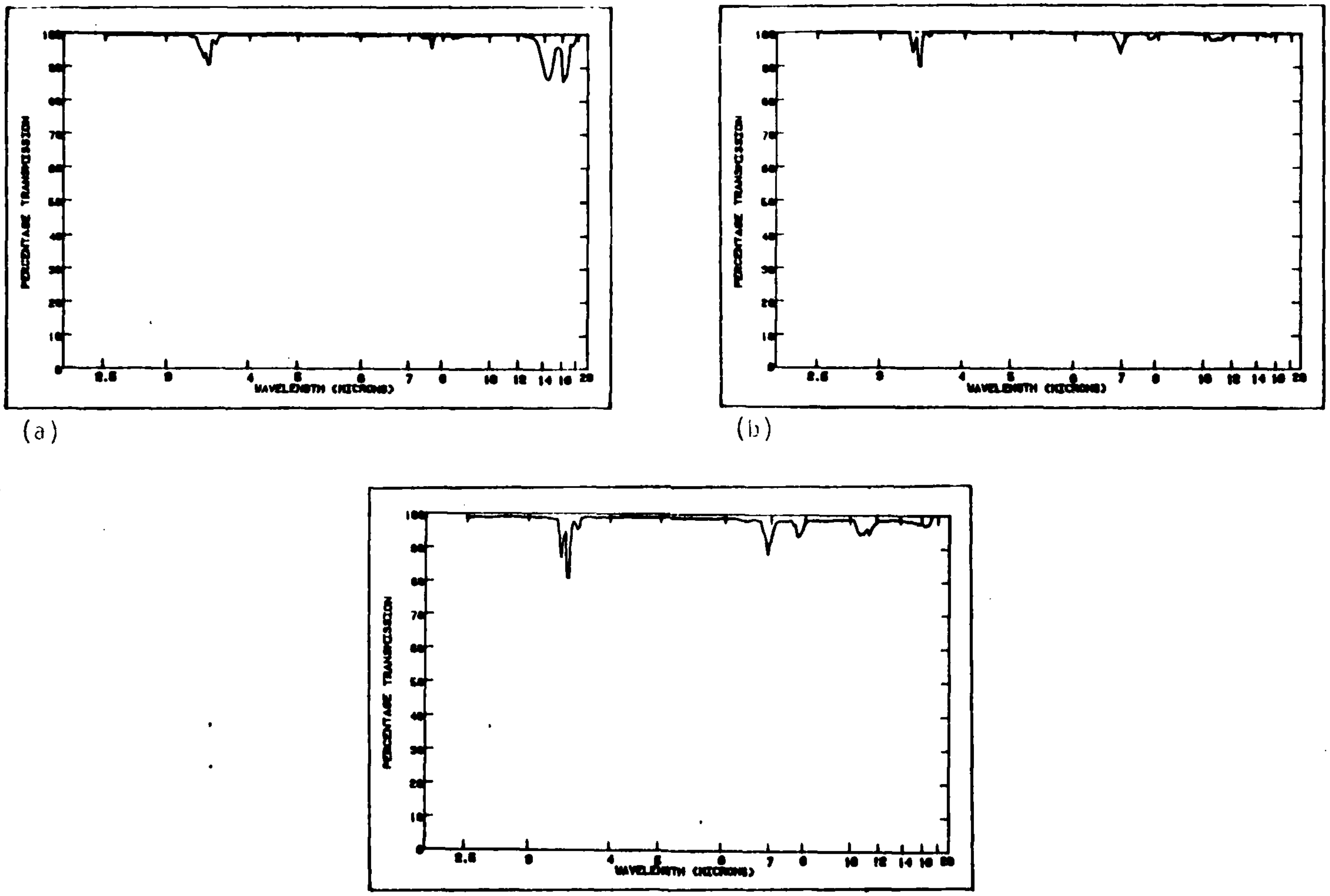


Figure 26. Transmission Spectra From 1.0 to 2.5 Microns of 10 Torr (3.22 x 10^{17} molecules/cm^3): (a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$ (c) Both $Zn(CH_3)_2$ and $Se(CH_3)_2$ (d) $Zn(CH_3)_2$ + 12 psi Ar (e) $Se(CH_3)_2$ + 12 psi Ar (f) Constuients of c + 12 psi Ar

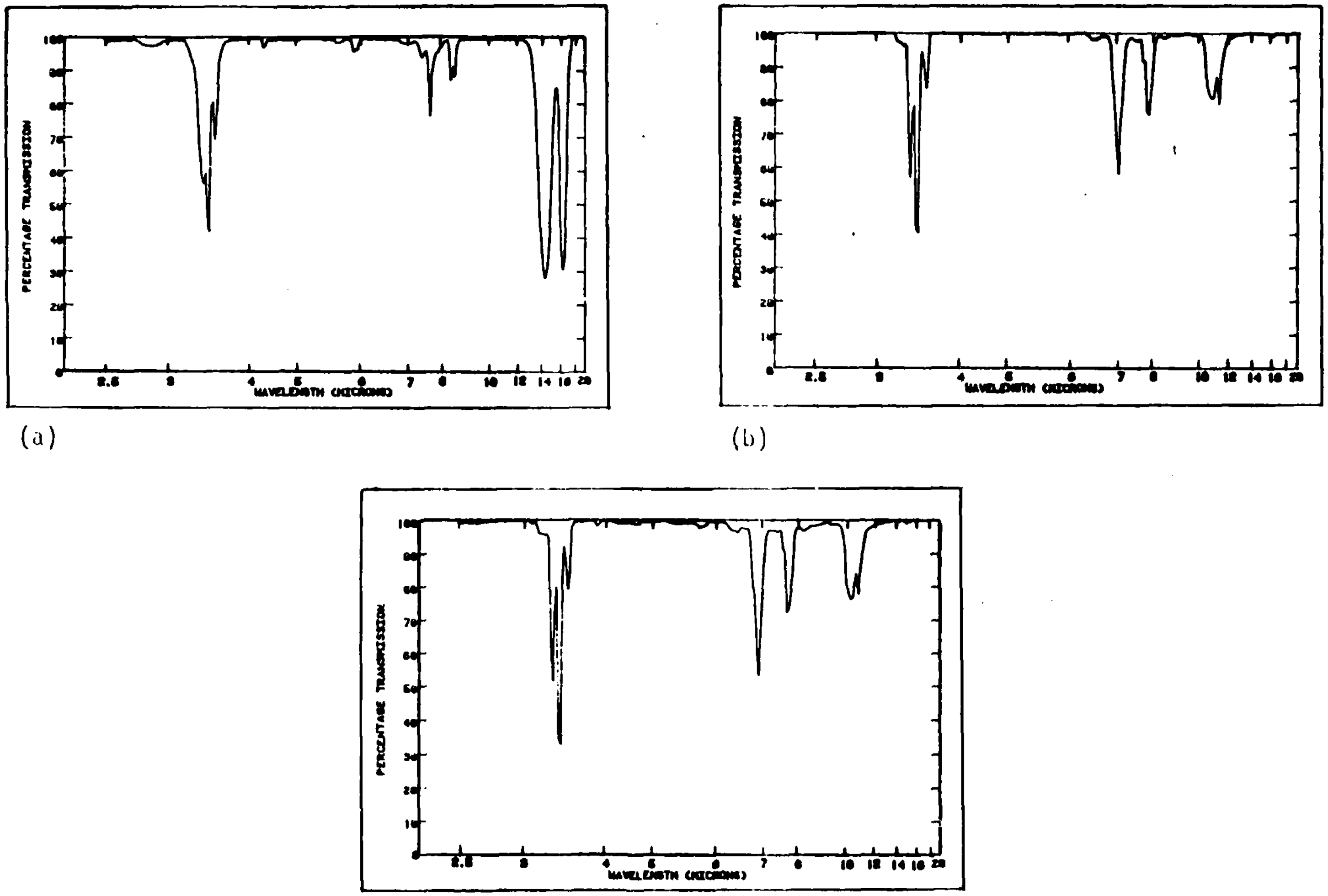


(a)

(b)

(c)

Figure 27. Transmission Spectra From 2.5 to 20 Microns of 10 Torr (3.22 x 10^{17} molecules/cm^3): (a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$ (c) Both $Zn(CH_3)_2$ and $Se(CH_3)_2$



(a)

(b)

(c)

Figure 28. Transmission Spectra From 2.5 to 20 Microns of 12 psi Ar Mixed with 10 Torr (3.22×10^{17} molecules/cm^3): (a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$ (c) Both $Zn(CH_3)_2$ and $Se(CH_3)_2$

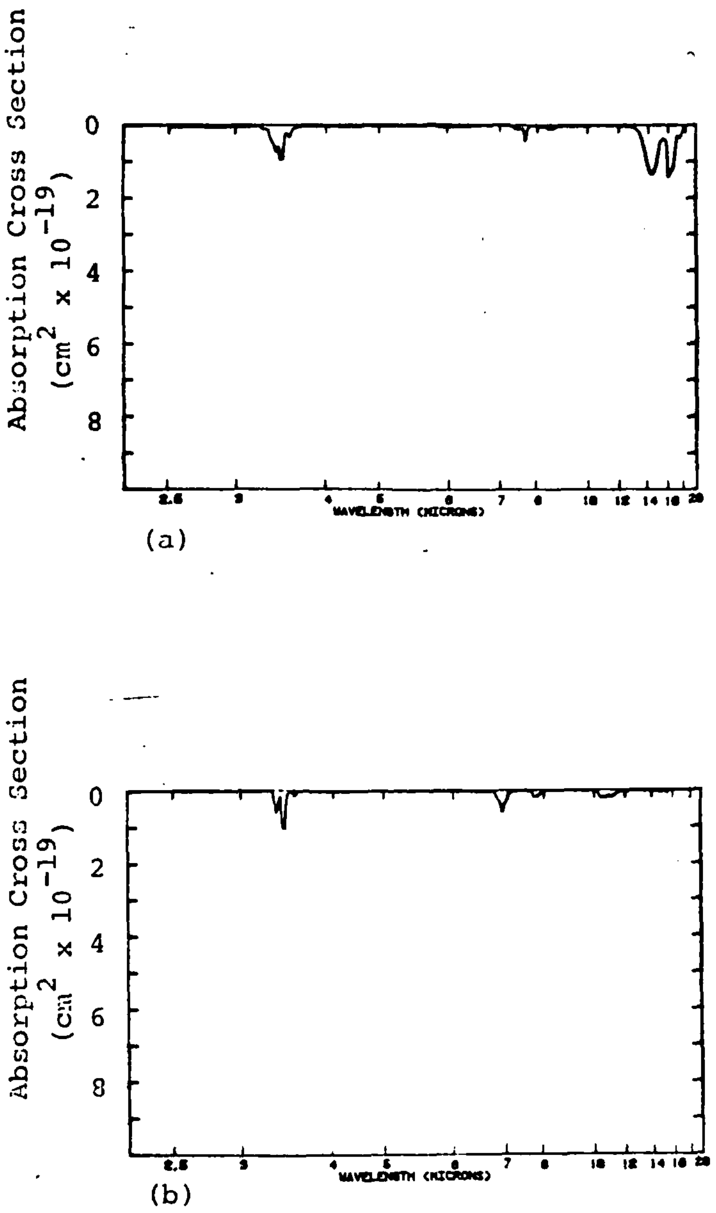


Figure 29. Infrared Absorption Cross Sections
(a) $Zn(CH_3)_2$ (b) $Se(CH_3)_2$

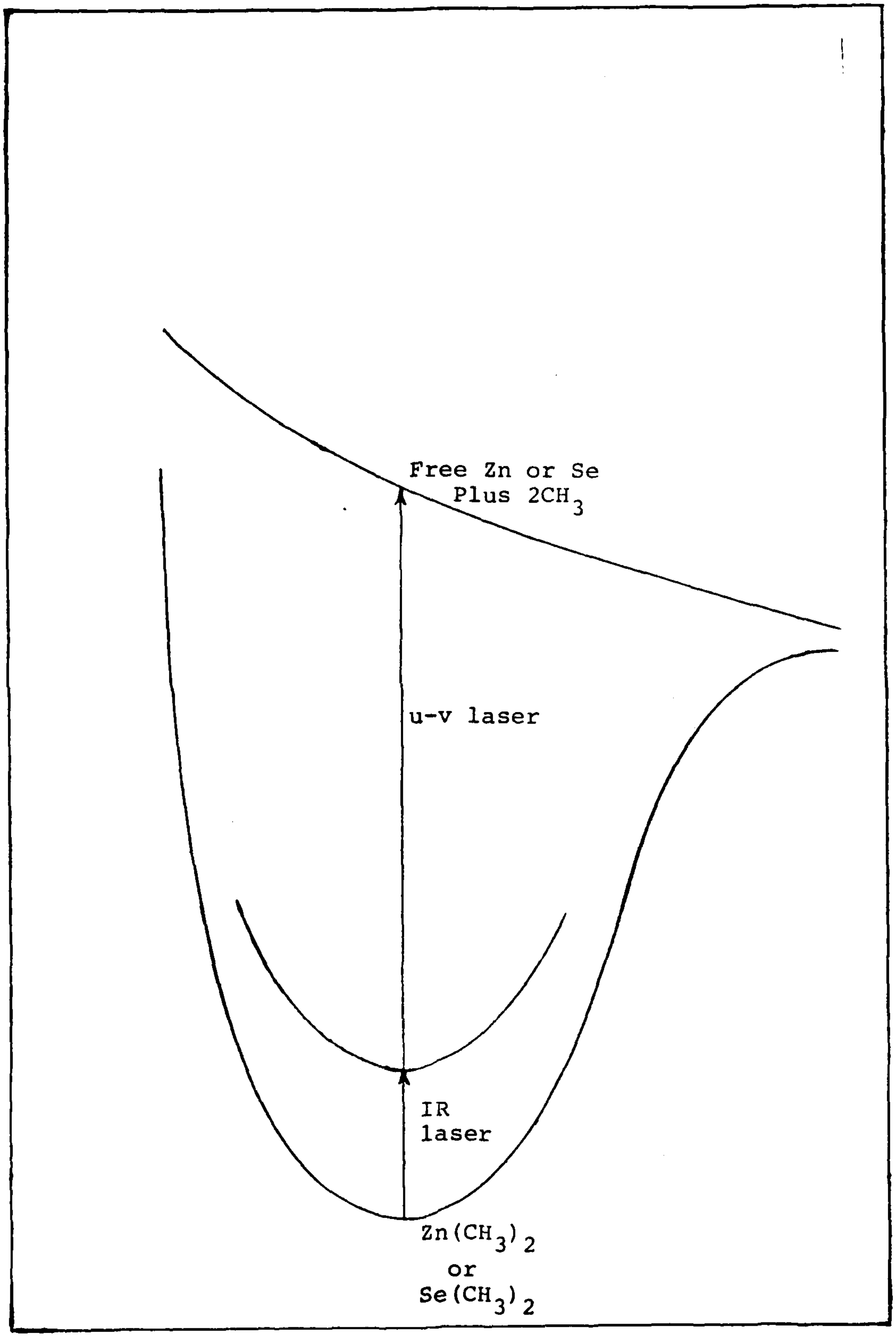


Figure 30. Two-Step Deposition Scheme

shown. For good selectivity of the elements, it is important to know the contribution of other molecules with similar characteristics to the molecules being used. Such molecules would be those which contain elements from the same family of the Periodic Table. For $Zn(CH_3)_2$, the other molecules are $Hg(CH_3)_2$ and $Cd(CH_3)_2$ while for $Se(CH_3)_2$, there exists $S(CH_3)_2$ and $Te(CH_3)_2$. In Figure 31, the absorption of the Group VIA molecules are shown (Ref 24). Unfortunately, such data is not available for the Group IIB organometallic molecules. Definite differences do exist indicating the high selectivity potentially achievable with this procedure.

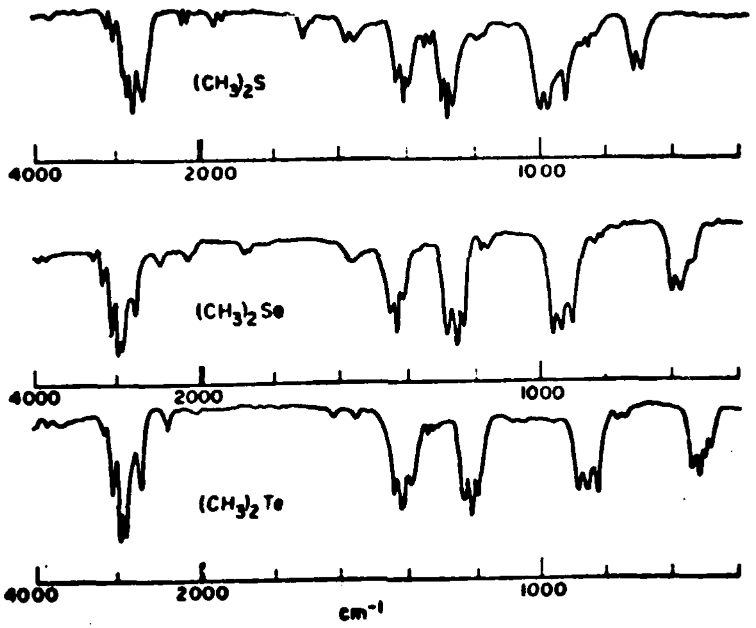


Figure 31. Absorption of the Group VIA Molecules

V Conclusions

Zn, Se, and ZnSe thin films (~ 100 to 6000Å thick) have been deposited on quartz and sapphire substrates with an incoherent Hg arc lamp u-v light source that photodissociates the organometallic molecules $Zn(CH_3)_2$ and $Se(CH_3)_2$. Deposition times were varied from one to four hours which resulted in films with diameters of approximately 1.5 cm. Such long times were required since the u-v light source output at the wavelengths required for photodissociation ($\lambda < 2420$Å) was very low, less than 10 watts over 2 cm diameters. These films were deposited by photodissociating the vapors of the organometallic molecules containing the elements Zn and Se. A scanning electron microscope was used to determine whether the elements were present in the films. Unfortunately, no elements below sodium on the Periodic Table could be detected by the microscope. For the surfaces analyzed, it was found that the zinc films contained only zinc and chlorine. Chlorine was used in the manufacturing of the samples of $Zn(CH_3)_2$ and is known to have an absorption peaked at 3300Å. Since the Hg u-v light source emits photons at 3300Å, free Cl atoms can simultaneously be deposited. Future experiments using an u-v laser instead of an incoherent u-v source should eliminate this Cl impurity. The selenium films contained only selenium.

A stylus was used to measure a zinc film's surface uniformity. The film's surface had a uniformity of 6%. Two factors contributed to the non-uniformity of the films. The substrates were used as supplied by the manufacturer and no attempts were made to improve their surface quality. Also, the incoherent light source did not emit a uniform beam. Therefore, the measured uniformity would not be the limit of this technique when a uniform laser beam is used on a prepared substrate.

Some films were deposited with a mask placed between the substrate and light source. The resulting films showed the outline of the mask. A zinc film was attempted to be deposited with BK-7 glass between the substrate and light source. This glass does not transmit radiation below 3400Å. Spectroscopic measurements showed that the threshold wavelength for the photodissociation of both Zn- and Se-$(CH_3)_2$ was approximately 2420Å. The attempted deposition of zinc using only radiation above 3400Å resulted in no visible film on the substrate. In addition, the substrate's heating had a maximum rise of only 5°C indicating no possible pyrolysis effects. <u>The small temperature rise of the</u>

substrate and lack of film deposition with the BK-7 glass provides experimental proof that u-v photons are the only effect producing the thin film depositions.

Previous experiments by other people have produced small area films (~ 1 mm^2 areas) consisting of only one atomic specie. However, this effort is the first demonstration of depositing large area films and two atomic species simultaneously.

Absorption measurements were made of the organometallic vapors $Zn(CH_3)_2$ and $Se(CH_3)_2$ from 0.2 to 20 microns. The measurements indicate the potential for a selective two step laser process to deposit the films. A CO(5.6 - 5.9μ) laser may be used to excite the $Zn(CH_3)_2$ and a CO_2(10.6μ) laser to excite the $Se(CH_3)_2$. A KrF (2480Å) laser would then be used to photodissociate the excited methyls containing the Zn and Se. The resulting films from laser photodissociation should be able to produce films with a purity not attainable with any of the other conventional deposition methods. This technique also promises a much improved control over the deposition as opposed to the presently used methods.

VI Recommendation For Future Work

In the course of completing any successful research many recommendations for future work can be made. This is particularly true for this research of the photodeposition of thin films. The following explains the future work which should be addressed.

A laser with $\lambda < 2420\text{Å}$ should be used to photodeposit Zn and Se thin films. A CW Ag^+ laser (Ref 43) or a frequency doubled dye laser could be used. Since $\lambda < 2420\text{Å}$, this process should eliminate any Cl impurities from being deposited.

A standard Rutherford backscattering technique should be used to determine whether any C or H impurities exist in the deposited films. The presence of these impurities in the films would be due to the trapping of free methyl radicals, which are liberated when the organometallics are photodissociated. Scavengers, such as cyclohexane could be used to eliminate the trapping of the methyl radicals in the films (Ref 41).

A two step process to photodissociate the organometallic vapors should be used to photodeposit a stochimetric film of ZnSe. This process would require three lasers, one u-v and two infrared lasers. A Co(5.6 - 5.9μ) laser would be used to excite the $Zn(CH_3)_2$ and a CO_2 (10.6μ) laser to excite the $Se(CH_3)_2$. A KrF (2480Å) laser would then be used to photodissociate the excited methyls containing the Zn and Se. The intensity of the two infrared laser beams could be varied to control the number of excited $Zn(CH_3)_2$ and $Se(CH_3)_2$ molecules. Since the excitation of the $Zn(CH_3)_2$ is independent of the excitation of the $Se(CH_3)_2$, a stochimetric ZnSe thin film could be deposited.

The physical mechanisms for depositions should be investigated. Issues not understood are: Do the zinc and selenium combine before or after impinging on the substrate? What is the crystal structure of a stoichiometric ZnSe thin film? To what degree does the substrate's crystal structure and surface flatness and cleanliness have on depositing stoichiometric films?

The possibility of depositing other materials as thin films via this method should be addressed. ZnSe and ZrO films would be good candidates to examine. Also, the potential of producing polished surfaces by "filling" holes via this deposition method should be investigated. And finally, would the laser annealing of the deposited film's surface benefit the quality of the thin films?

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Appendix A: List of Symbols

E_d	desorbed atom's energy after equilibration with the substrate (joules)
E_r	desrobed atom's energy before equilibration with the substrate (joules)
E_v	vapor atom's incident kinetic energy (joules)
ΔG_{des}	activation energy for the desorption process (joules)
h	Planck's constant (joule sec)
I	Intensity (watts/cm^2)
k	Boltzman's constant (joules/°K)
p	pressure (torr)
R_d	dissociation rate (1/sec)
T	temperature of organometallic compound (°K)
T_a	temperature of an atom on a substrate (°K)
T_d	desorbed atom's temperature after it equilibrated with the substrate (°K)
T_r	desorbed atom's temperature before equilibration with the substrate (°K)
T_s	substrate's temperature (°K)
T_v	vapor atom's incident temperature (°K)
α_T	thermal accommodation coefficient (unitless)
ν	frequency of light (hertz)
ν_a	frequency at which the absorbed atom attempts to desorb (hertz)
σ_d	absorption cross section (cm^2)
τ_s	atom's time on substrate's surface (sec)

Vita

Walter E. Johnson was born on 20 July 1953 in Roslyn, New York. He is the son of Mr. and Mrs. Walter O. Johnson of Bluffton, Indiana. He graduated from Northeast Senior High School, Saint Petersburg, Florida in 1971. He attended the University of South Florida, Tampa, Florida, from which he received the degree of Bachelor of Science in Materials Engineering in 1975. He was employed as a plant engineer for Indiana General, Valporaiso, Indiana. He worked at the Air Force Materials Laboratory from February 1977 until he entered the Air Force Institute of Technology on June 1979.

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High purity Zn, Se, and ZnSe thin films (~ 100 to 6000Å thicknesses) have been deposited on both quartz and sapphire substrates by using a Hg arc lamp u-v light source to photodissociate the organometallic molecules $Zn(CH_3)_2$ and $Se(CH_3)_2$.

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Large area depositions (~ 1.5 cm diameter circles) have been produced, along with masked depositions created by selectively blocking the incoherent light source. Absorption measurements of these organometallic vapors from 0.2 to 20 microns indicates the possibility of producing ultra-high purity thin films by using simultaneously both a CO (5.6 - 5.9μ) and a CO_2 (10.6μ) laser in conjunction with a pulsed KrF (2480Å) in a highly selective two step photodissociation process. Such results offer the potential for a drastically new and greatly improved quality film plus an extremely well controlled alternative to the more conventional thin film deposition techniques such as thermal vacuum deposition, sputtering, and chemical vapor deposition.

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