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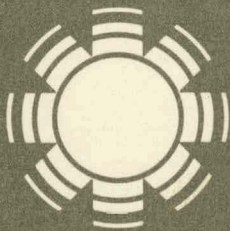
SERI/TP-31-064

November 1978

Department of Energy
Contract No. EG-77-C-01-4042

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Apparatus for Simultaneous Measurement of Mass Change, Optical Transmittance, and Reflectance of Thin Films



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SERI/TP-31-064
UC CATEGORIES: UC62E, UC63E

APPARATUS FOR SIMULTANEOUS MEASUREMENT
OF MASS CHANGE, OPTICAL TRANSMITTANCE,
AND REFLECTANCE OF THIN FILMS

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NOVEMBER 1978

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Prepared for the
U.S. Department of Energy
Division of Solar Technology
Under Contract EG-77-C-01-4042

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PREFACE

This report was prepared in compliance with the provisions of Contract No. EG-77-C-01-4042. The work has been carried out in support of the Surfaces and Interfaces Task (FY 78 AOP-3109) in the Research Division of the Solar Energy Research Institute (SERI).

The report was prepared by Alvin W. Czanderna of SERI and Eric Prince and H. F. Helbig of Clarkson College of Technology. Construction of the apparatus described was begun in the summer of 1976 by Mr. Prince--a doctoral student in Physics. In May of 1978, SERI subcontracted support for the project with H. F. Helbig as a principal investigator at Clarkson and A. W. Czanderna as the SERI collaborator.

The authors are pleased to acknowledge the sources of support for this project; namely, Clarkson College, Ultramicrobalance Instruments, the American Vacuum Society, and the Department of Energy through a prime contract to the Solar Energy Research Institute. The assistance of M. Gutierrez and P. Russell in securing the SEM photographs and J. Mott for the ISS depth profile is appreciated.

The equipment provides a unique capability for studying the preparation and reactive degradation of copper sulfide and black chrome.



A. W. Czanderna, Task Leader
Surfaces and Interfaces
Materials Branch

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ABSTRACT

An apparatus consisting of a vacuum ultramicrobalance and optical equipment for measuring transmittance and front surface reflectance of thin films from 400 to 800 nm is described. Thin films formed on substrates by thermal or reactive evaporation can be heated in reactive gases of different compositions and pressures. As the chemical composition of the film changes, the optical changes in the film can be monitored simultaneously using computerized data collection, control, and analysis. Representative results obtained for the preparation of a $\text{Cu}_{1.63}\text{S}$ film on a sapphire substrate and its reaction with oxygen are presented along with ion scattering profiles, SEM, and structural data taken after the film was removed from the microbalance.

Section I

INTRODUCTION

The importance of the simultaneous measurement of mass change of a sample and at least one other parameter has been summarized in recent review articles [1,2,3]. Infrared spectroscopy has been the most widely used additional parameter, but has required using materials with large surface areas [4]. Studies combining mass change with optical characterization in the ultraviolet (UV) and near infrared (IR) have been rarely used, even though Wieder and Czanderna showed that important information could be gained about the reactions of thin films. In addition to showing that copper films can be oxidized to a gross defect phase, $\text{CuO}_{0.67}$ at temperatures of 110-200°C [5], their initial work was extended to determine the optical constants of $\text{CuO}_{0.67}$ [6], and the reactivity of copper single-crystal films grown on sodium chloride substrates [7,8].

In the previous work by Czanderna and his co-workers, an apparatus was used that permitted the simultaneous measurement of mass change and optical transmittance of a thin film. The apparatus has been modified and improved several times, but new capabilities were not added. In this paper, a complete description will be given for an apparatus that has evolved from the one previously described [5], but which includes the ability to measure the transmittance, T , and front surface reflectance, R , of thin films in addition to their mass change. The succession of improvements to the original apparatus, reported in various publications dealing with the results obtained with the equipment, are consolidated into the description below. The availability of inexpensive microprocessors that can be used for remote control, data collection, and analysis has greatly simplified the data gathering and reduction processes. The measurement of both T and R also permits study of the thickness dependence of the optical constants, n and k [9], during the formation of a reaction product on a thin film.

With the apparatus, thin metal films are evaporated onto substrates suspended from a microbalance. These films are then exposed to a reactive atmosphere in situ. During the reaction process, the effective stoichiometry of the sample is determined from the microgravimetric data while the optical transmittance and reflectance of the sample are simultaneously monitored with a computerized detection system. Auxiliary studies of the films, made after removal of the film from the balance, include ion scattering spectrometry, scanning electron microscopy and electron diffraction. The T and R data can also be used as "fingerprints" for correlating the extent of a reaction on films prepared in auxiliary vacuum systems. If the prepared films are found to be suitable with regard to continuity, grain size and composition, the optical constants of these films are determined from the T and R data [5,6]. On samples found to be unsuitable for the determination of the optical constants, the measured T and R still give considerable insight into the film formation process [7,8].

The system described below allows a unique approach to the study of the formation and reaction of Cu_xS and the degradation of black chrome, both important solar energy materials. To demonstrate the utility of the apparatus, data on a representative $\text{Cu}_{1.63}\text{S}$ sample prepared and studied on this system are presented and discussed.

Section II

APPARATUS AND PROCEDURES

The apparatus used for the simultaneous measurement of mass change, optical transmittance, and reflectance of thin films is shown schematically in Fig. 1. The principal components of this apparatus are a substrate (A); an automated ultramicrobalance (B), a stainless steel and glass very high vacuum system, which includes a deposition assembly for evaporating thin films onto substrates suspended from the microbalance and is connected to a very high vacuum (VHV) gas handling station (C); an optical system for determining the transmittance and reflectance of films on the substrate, and a hinged tube furnace (D) for heating the sample.

MASS MEASUREMENTS

Mass changes are determined using a bakeable high load pivot-type quartz beam vacuum ultramicrobalance. Details of the construction, calibration, and limitation of this type balance have been described [10]. The all-quartz balance is inert and may be baked to 400°C. Typical operating characteristics of the balance include a reproducibility of ± 0.1 g, a period of 14 sec, and a sensibility of ± 0.2 g in high vacuum. During studies in reacting gases, the sensibility may reach ± 0.5 g due to buoyancy and thermomolecular flow effects [11].

Automatic operation of the balance is achieved using a transducer (E), magnetic compensation (F) [12], and a mechanical servo feedback circuit [13]. A 12.32 mm length of 0.787 mm diameter piano wire (G) serves as a probe attached to the quartz hangdown fiber. The probe is centered inside the JC-2-0.25 transducer powered by a model 83 type F translator (H), both manufactured by the Crescent Engineering and Research Company. In automatic operation, the balance beam moves the piano wire probe inside the transducer and causes an imbalance in an ac bridge circuit formed between the transducer and translator. A signal from the translator proportional to the amount of imbalance of the bridge circuit is amplified (I) and used to drive a servomotor (J). The action of the servomotor on a 1000 40 turn model E helipot (K) results in a change in the current through a solenoid (F), restoring the balance to the null position and changing the voltage drop across a standard resistor (L). The latter voltage is recorded after being reduced to between 0 and 1 mV by two bucking voltage sources (M), acting as an autoranging device [14].

The transducer, which is external to the vacuum system, surrounds a grounded 3.175 mm o.d. - 3.023 mm i.d. silver tube through which the hangdown fiber with the piano wire probe passes. The silver tube provides an electrical ground that eliminates electrostatic interactions between the quartz-enclosed probe and vacuum wall and minimizes thermal gradients inside the stainless steel core of the transducer.

Horizontal forces which act on the probe in the transducer core at zero vertical pull are small for a translator with a 10 kHz frequency. These are

easily overcome by the combined weight of the quartz-encased Cunife compensation magnet (N) located below the piano wire probe on the hangdown fiber and a gold tare hung on the fiber below the magnet. Enough tare is used to counterbalance substrates to within the 10 mg automated range of the balance.

For the current study of copper sulfide thin films, sapphire substrates (A), 1 mm thick, 37 mm in diameter, and weighing approximately 4.2 g are suspended from the balance (B) as shown in Fig 1. The substrate is held in a horizontal position by a support composed of 1 mm o.d. quartz rod. The support consists of a "Z" in the horizontal plane with a 10 mm vertical length of quartz rod attached to the center of the "Z" at one end and a quartz hangdown fiber on the other. For holding the substrate, this vertical length is inserted into a 1 mm i.d. hole in the center of the substrate. Another fiber suspended from the balance beam provides a convenient hook for holding the substrate support fiber and quartz tare weights used to compensate for minor mass differences between substrates. A new substrate is used for each film studied.

VACUUM SYSTEMS

The microbalance is mounted in a glass housing (O) containing a quartz window (P_1) and the connection (C) to the glass and stainless steel high vacuum station. The latter is used to pump the system to ca. 10^{-3} Pa before using a 15 l/s vac-ion pump (Q) attached to one end of the balance housing through a stainless polyimide valve (R) and stainless steel bellows (S). With this pump, the system pressure can be reduced to 3×10^{-6} Pa without baking. Stainless steel "Conflat" type vacuum flanges with copper gaskets are used throughout, with the exception of one flange, T, which has been sealed permanently with a gold "O" ring. A stainless steel hangdown tube (U), which surrounds the sample suspended from the microbalance, contains a six-way cross near its base. A quartz window (P_2) is mounted onto the bottom port. The four horizontal ports hold a push-pull deposition boat assembly (V), a push-pull boat shield assembly (W), a pyrex window (X) and an access port (Y); the latter is used to load charges into the deposition boat.

The VHV station connected at (C) has been described in detail recently [15]. This system contains a diaphragm manometer and thermocouple gages for monitoring the pressure in the balance chamber. Pressures below 10^{-1} Pa are read with a Huntington 4336P ionization gage. The gases used in the balance system are stored, mixed in, and admitted through this station. Vacuum in the station is produced with a zeolite-trapped, glass, three-stage oil diffusion pump and a mechanical forepump. The balance system is normally pumped from atmospheric pressure to below 5×10^{-4} Pa with this station before using the vac-ion pump (Q). A modest bakeout of the system, is accomplished using heating tapes, the tube furnace (D) and a heat gun.

OPTICAL MEASUREMENTS

The optical system is designed to take in situ transmittance and front surface reflectance measurements. Back surface reflectance measurements are also taken, but their quantitative value is considerably limited because light

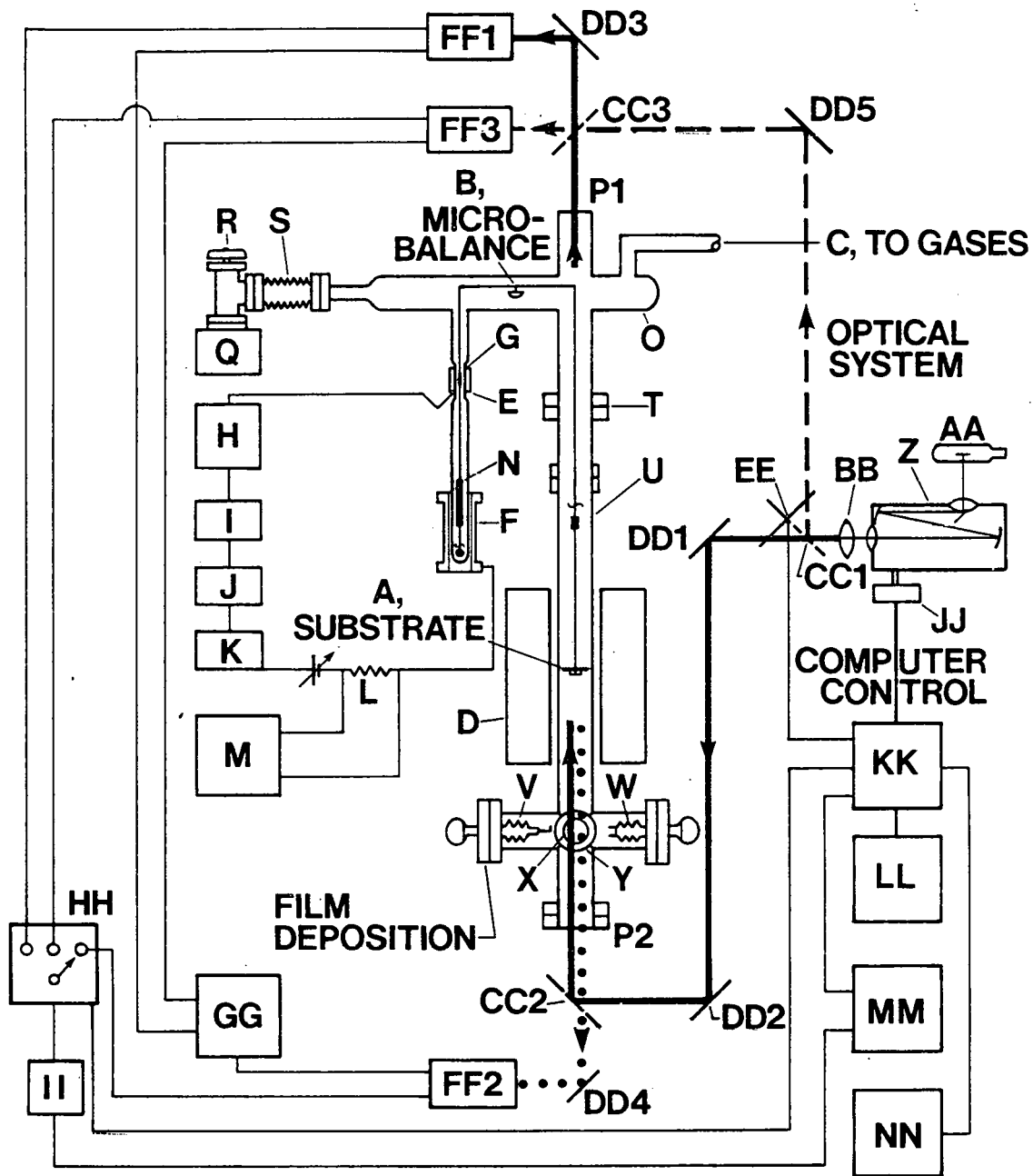


Figure 1. Apparatus for the Simultaneous Measurement of Mass Change, Optical Transmittance and Reflectance.

A-substrate; B-ultramicrobalance beam; C-to VHV system; gases and gages; D-furnace; E-transducer; F-magnetic compensation solenoid; G-piano wire probe; H-translator; I-amplifier; J-servo motor; K-helipot; L-standard resistor; M-bucking voltage source and recorder; N-cunife compensation magnet; O-glass balance housing; P1, P2-quartz windows; Q-ion pump; R-stainless valve with polyimide gasket; S-stainless steel bellows; T-flange with gold "O"-ring; U-stainless steel hangdown tube; V-push-pull deposition boat assembly; W-push-pull boat shield assembly; X-pyrex window; Y-access port (rear); Z-monochromator; AA-light source; BB-lens; CC1-CC3-beam splitters; DD1-DD5-full silvered mirrors; EE-beam selector; FF1-FF3-photomultiplier tubes (PMT); GG-high voltage PMT supply; HH-PMT tube selector; II-photometer; JJ-motor driven wavelength drum; KK-microprocessor; LL-input/output terminal; MM-digital volt meter; NN-x,y-recorder.

scattered by the microbalance beam and tare weight on the suspension seriously attenuates the signal. The optical paths for the T and R measurements are shown in Fig. 1.

Monochromatic light (400-800 nm) is obtained using a Bausch and Lomb grating monochromator (Z) with a ribbon filament tungsten light source (AA). Light from the exit slit passes through an achromatic lens (BB) where it is focused upon the sample (A). A beamsplitter (CC1) divides the light beam into two optical paths of the same length. Care was taken to limit the maximum beam diameter inside the balance system between the optical windows (P_1 , P_2) to prevent any beam contact with the walls. A rigid optical bench holds upper and lower tracks to support most of the optical components. A mirror (DD1) and beam-splitter (CC1) are mounted on the balance table along with an achromatic field lens (BB). A computer-controlled beam selector (EE), which is attached to a nearby wall to keep vibration away from the microbalance table, is used to direct one beam through the system while suppressing the other. In one position, the light passes through a beamsplitter (CC1), reflects off two mirrors (DD1, DD2) and another beamsplitter (CC2), and passes up through a quartz window (P_2) to the sample (A). Light transmitted through the sample (heavy solid line in Fig. 1) continues through a quartz window (P_1) and beamsplitter (CC3) where it is directed onto a photomultiplier (FF1) by a mirror (DD3). Light reflected from the sample (dotted line) passes back through a quartz window (P_2), and through a beamsplitter (CC2) where it is reflected from a mirror (DD4) onto a photomultiplier (FF2). In the other beam selector position, light reflected (dashed line) off a beamsplitter (CC1) and a mirror (DD5) passes through another beamsplitter (CC3) onto a photomultiplier (FF3) to monitor the spectral intensity of the light source.

All data are normalized with the source output to correct for changes in spectral intensity over the 400-800 nm interval. All three RCA 6217 photomultiplier tubes are powered by a Fluke model 413C high voltage DC supply (GG). Photocurrents from these tubes, chosen by a computer-controlled signal selector (HH), are detected and amplified using a solid state photometer (II) [16]. A motor-driven wavelength drum (JJ) on the monochromator (Z) is geared to a potentiometer to provide an output voltage proportional to the wavelength.

Selection of the photomultiplier tubes, control of the beam selector, advance of the wavelength drum, wavelength determination, data collection, analysis and printout are all accomplished with an IMSAI 8080 microcomputer (KK) and LA 36 DEC-writer II terminal (LL). The data from the photometer is interfaced with the computer through a digital voltmeter (MM) and the reduced data are plotted on an X-Y recorder (NN). For the wavelength spectrum of 400-800 nm, 21 sets of T and R data are routinely obtained at 20 nm intervals in 20 minutes.

Careful positioning of the substrate holder in the horizontal plane is necessary to prevent it from interfering with the light path through the sample. This is accomplished by appropriately aligning the direction of the hook on the substrate support fiber prior to hanging the substrate from the balance suspension fiber. To characterize the substrate and optical windows and to account for all scattering from the microbalance and substrate suspension components, two blank runs are necessary prior to evaporation of a

film. With these calibration data, the T and R of an evaporated film can be measured at selected intervals during its preparation, or continuously when reacting with the environmental gases. The optical properties of the film can be calculated from the measured values of T and R by the methods described by Nilsson [9].

PREPARATION OF FILMS

To prepare a copper film, the push-pull deposition boat assembly (V), consisting of two 6.25 mm copper feedthroughs and a molybdenum boat, is pushed into the center of the hangdown tube (U). A stainless steel shield attached to the assembly below the boat prevents deposition onto the optical window (P2). Prior to deposition, the boat and deposition charge are degassed by heating. During this process, the substrate is protected by the push-pull boat shield (W). The charge in the boat is resistively heated using a low voltage, high alternating current obtained from a saturable core transformer. The 28 cm distance from the boat to the substrate results in a film uniformity of about 1%. The system pressure rises continuously during deposition, but is not allowed to exceed 5×10^{-4} Pa. The film thickness depends on the material being deposited and the time the evaporation boat is cyclically heated. Typically, films from 5-80 nm may be prepared before cooling the boat. Thicker films can be prepared by repeated deposition.

As the charge is heated, onset of deposition is observed as an apparent mass loss on the microbalance, which results from the momentum transfer of the impinging evaporant. When the deposition is terminated, the microbalance provides the net mass gained from the evaporation. During deposition, the offset of the balance from the momentum transfer remains approximately constant so that if the density of the deposited material is known, films of a desired thickness can be prepared to within a few tenths of a nanometer by using the total mass gained during the deposition.

TEMPERATURE CONTROL AND MEASUREMENT

The apparatus is housed in an insulated room, 2.44 x 2.44 m, maintained at a constant temperature to within $\pm 0.2^\circ\text{C}$ by thermostatically controlled heaters. A 50.8 mm diameter hinged tube furnace (D) which surrounds the substrate region of the hangdown tube is used to heat the substrate to temperatures from 25° to 600°C . The furnace temperature is determined by using 10 chromel-alumel thermocouples cemented around its inner wall in the horizontal plane of the sample. Prior to film studies, the sample temperature and its horizontal temperature gradients were correlated with the furnace temperature using a chromel-alumel thermocouple located inside the hangdown at or near the sample position, while the system was filled with nitrogen or hydrogen, or was under vacuum.

MATERIALS

Materials in use for the current study on the preparation and the characterization of copper sulfide thin films include: 99.999% pure copper from Leico Industries (for thermal evaporation); c.p. grade hydrogen sulfide from Matheson Gas Products; research grade hydrogen in 1-liter break seal flasks from Airco Industrial Gases; dry grade nitrogen from the Linde Division of Union Carbide; 99.6% pure potassium permanganate for thermal decomposition to produce oxygen from J. P. Baker Chem. Co.; molybdenum deposition boats from R. D. Mathis Co.; and sapphire substrates from Crystal Systems, Inc.

FILM-GAS REACTION PROCEDURE

When a copper film of the desired thickness has been deposited, the vacuum pump is isolated by closing the valve R. After the sample is brought to the desired reaction temperature, hydrogen gas is slowly admitted through C into the balance chamber from the VHV system until a final pressure of 13.3 kPa is reached. While the balance establishes a well-defined baseline, the VHV station is isolated from the balance chamber, pumped to below 1×10^{-3} Pa, and refilled with 13.3 kPa of an H_2S/H_2 gas mixture. The composition of this mixture is chosen to provide the final H_2S/H_2 ratio desired after mixing with the H_2 in the balance chamber. The reaction is started by opening the valve connecting the balance and the VHV station. With equal pressures on either side of the valve, no measurable buoyancy effects occur and the initial stages of the sulfurization reaction are easily observed. The mass change during sulfurization or other subsequent reactions is recorded continuously as a function of time, and the T and R of the film are measured at intervals consistent with the reaction rates, which vary from a few hours to a few weeks.

Section III

TYPICAL DATA

As part of a program to prepare and characterize Cu_2S thin films, copper sulfide (Cu_xS) thin films are being prepared and studied in this system. Data from a representative $\text{Cu}_{1.63}\text{S}$ film are presented here to illustrate the versatility of the apparatus for the characterization of thin films when combined with the auxiliary studies--ISS, SEM, and X-ray and electron diffraction.

Microgravimetric data are plotted in Fig. 2a for the sulfurization of a 61.2 nm thick copper film at 26°C in a 13.46 kPa $\text{H}_2/\text{H}_2\text{S}$ (initially, 39:1) gas mixture. This film was chosen for presentation because its slow reaction rate allowed numerous sets of optical data to be taken during the sulfurization process. The film reached an effective stoichiometry of $\text{Cu}_{1.63}\text{S}$ upon termination of the reaction, which was still incomplete after 508 hours. The arrows along the curve indicate times during the reaction process when optical data on the film were taken. Figures 2b and 2c show the transmittance and reflectance of the film for normal incidence corresponding to these times. The reflectance curves in Fig. 2c were scaled using published optical constants for copper [17]. It is apparent by comparison of the first optical data set (Curve 1, Figs. 2b and 2c) with that of the initial copper film that dramatic optical changes in the film take place early in the reaction process. In agreement with the gravimetric data, comparison of the T and R of Curve 8 with other fully sulfided Cu_xS samples and with Cu_2S curves derived using published optical constants [18] showed that the film was not completely sulfided. More data is needed on the optical changes in the Cu_xS films during their growth process before a complete interpretation of the results can be made.

Prior to the auxiliary studies, this film was exposed to an 81.31 kPa O_2/N_2 (1/3.7) gas mixture for 74 hours at 66°C. Depth profiles of the film were taken in a 3M Ion Scattering Spectrometer with a cylindrical mirror analyzer using a mixed ^3He (6.7×10^{-3} Pa): ^{20}Ne (2.7×10^{-3} Pa) target gas at a target current of 6nA. Figure 3a shows a depth profile taken with the ISS mini-beam. This beam probes much smaller film areas (10^{-4} cm²) than the optical system (1 cm²) and allows profiling different regions of the area sampled optically to search for possible lateral heterogeneity.

In Fig. 3b, the SEM photograph shows the topographical features of the film. No discontinuities or voids were observed in the film. A surface roughness is evident with a period of about 20 nm. Calculation of the film thickness depends on the extent of reaction and the number and amount of the various sulfide phases formed. A 122 nm thick film of pure Cu_2S will be formed from 61.2 nm of copper.

X-ray and electron diffraction data taken on the sample provide evidence for the existence of Cu_2S , CuS , and possible other intermediate phases. The presence of more than one sulfide phase complicates the correlation between the gravimetric and optical data, since three or more absorbing materials (Cu_xS , Cu_2S and Cu) are present simultaneously.

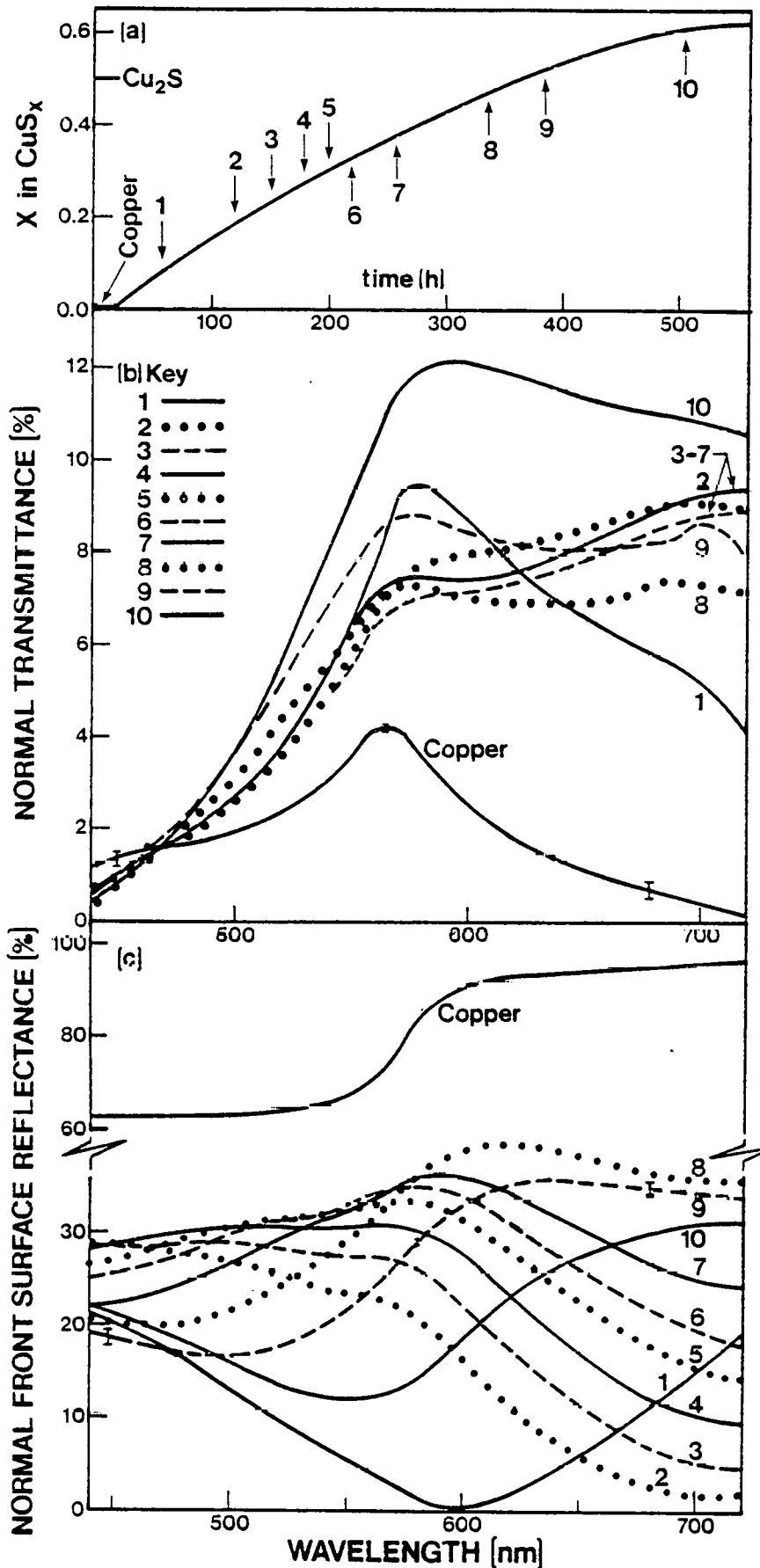


Figure 2. The Transmittance and Reflectance of a 61.2 nm Thick Copper Film at Various Stages of Sulfiding to Reach $CuS_{0.61} (Cu_{1.63}S)$ as shown by the Gravimetric Data.

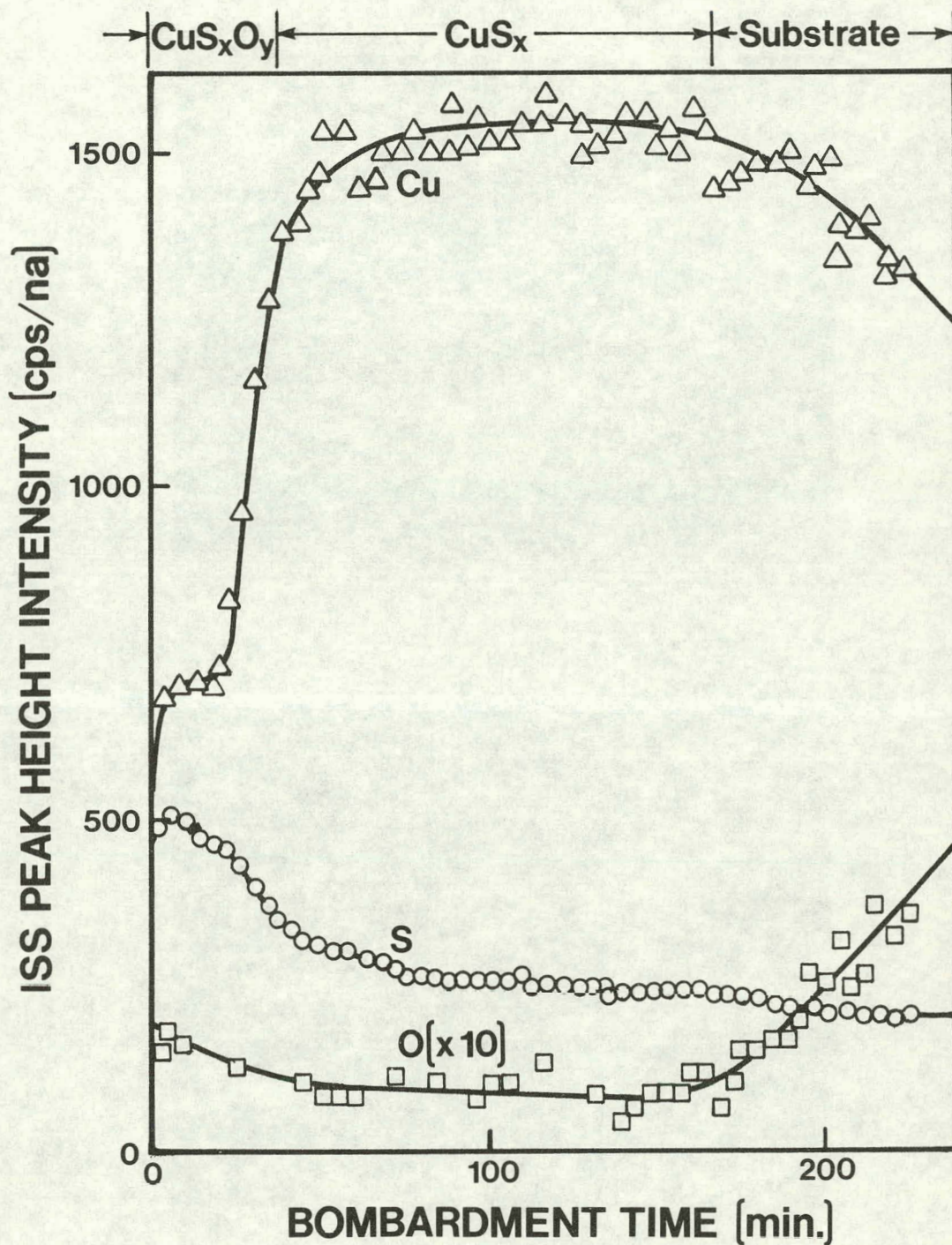


Figure 3(a). ISS Depth Profile of the Film Shown in Fig. 2. The film was exposed to 13.3 kPa of oxygen at 66°C for 16 hours prior to removal from the microbalance.

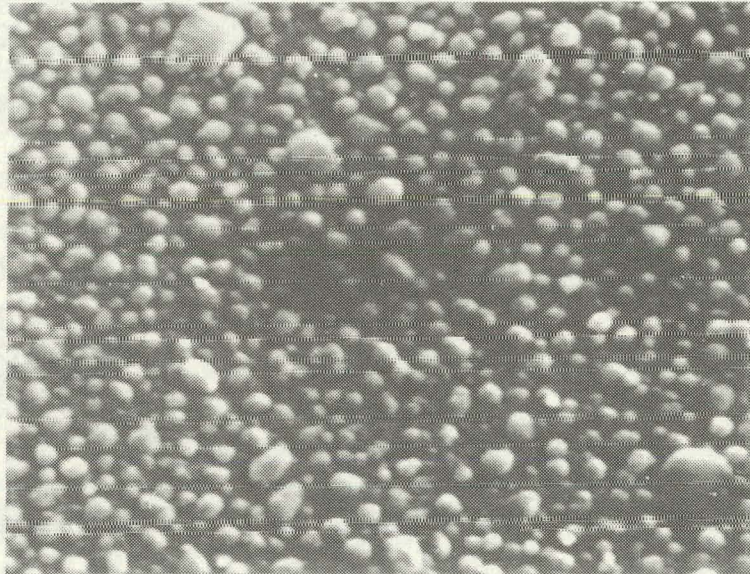
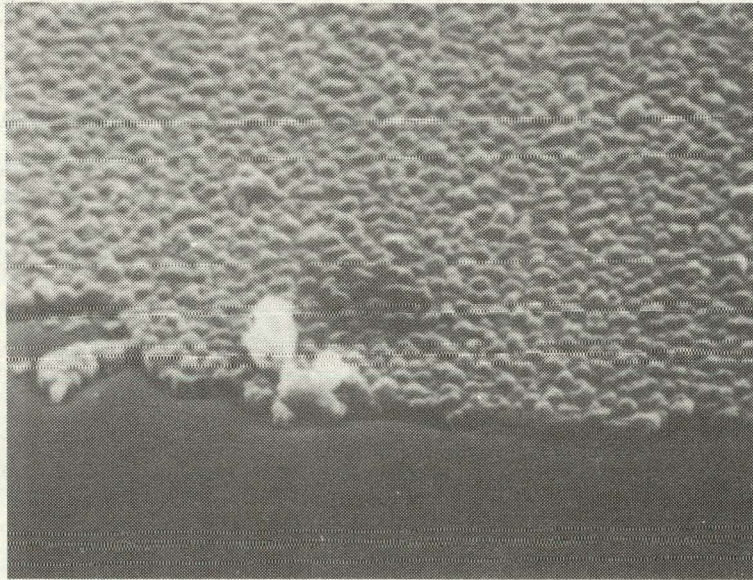


Figure 3(b). SEM photographs of $\text{Cu}_{1.63}\text{S}$.

Section IV

DISCUSSION

Even though the film described above was not allowed to sulfide to completion, useful optical information was obtained during the reaction process. Films allowed to sulfide to completion are continuous, and offer additional optical information when a single growth phase is present (as verified by the auxiliary measurements). For these films, the optical constants of the material (n, k) can be calculated from the transmittance and reflectance data at various stages of the sulfurization reaction and will provide important insight into the formation of the sulfide. For example, the change in these optical constants with film thickness can be studied, and the optical band gap and its temperature dependence for any stable or metastable composition can be calculated. Efforts are continuing to identify the conditions required to prepare and characterize thin films consisting of only polycrystalline Cu_2S .

Future work with the apparatus will include a study on the preparation and characterization of reactively evaporated black chrome, a selective solar energy absorbing material. For this study, the wavelengths of interest range from 300 to 2600 nm, but with much broader bandwidths at each wavelength. A dispersion monochromator, toroidal mirrors, and other equipment needed for the modification have been identified.

In conclusion, the capabilities of the apparatus have been demonstrated. Important results on the changes in composition and optical properties during reactions by thin films are anticipated.

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