260
3-26-81
JWA

(2)

DL-2467

SERI/PR-9237-1-T1

AMORPHOUS THIN FILMS FOR SOLAR CELL APPLICATIONS

Technical Progress Report for Period July 15—October 10, 1980

MASTER

By
A. D. Jonath
W. W. Anderson
J. L. Crowley
H. F. MacMillan, Jr.
J. A. Thornton

October 10, 1980

Work Performed Under Contract No. AC02-77CH00178

Dist-201
NTIS-22

Lockheed Missiles & Space Company, Inc.
Palo Alto Research Laboratory
Palo Alto, California

U.S. Department of Energy

Solar Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A03
Microfiche A01

AMORPHOUS THIN FILMS FOR
SOLAR CELL APPLICATIONS

LMSC-D767125

10 October 1980

Technical Progress Report
For Period 15 July 1980 to 10 October 1980

A.D. Jonath
W.W. Anderson
J.L. Crowley
H.F. MacMillan Jr.
J.A. Thornton (TelicCorp.)

Work Performed Under Contract SERI-XS-0-9237-1

LOCKHEED MISSILES & SPACE COMPANY, INC.
Palo Alto Research Laboratory
3251 Hanover Street
Palo Alto, CA. 94304

OVERVIEW

This report concentrates on a series of experiments performed (1) to develop successful back-layer contacts for a MIS solar cell and (2) to study the effects of argon inclusion on the properties of the active intrinsic layer in the a-Si:H cell. Mixtures of argon (Ar), phosphine (Ph_3), and hydrogen (H_2) were used at various partial pressures to assess the effectiveness of doping with a reactive gas. The inclusion of argon in d.c. reactively-sputtered films was measured using specially prepared "cathode image" samples and the results correlated with the SiH_2/SiH ratio in the films.

Section 1

BACK CONTACT LAYER DEVELOPMENT

In order to develop an efficient solar cell, it is necessary to limit the back contact resistance to below 1 ohm-cm^2 . Ohmic contact must be made with the highly resistive intrinsic layer. This can be achieved by preparing a highly doped n^+ contact layer with the use of reactive gas-phase doping. We began the development of such a layer using a mixture of Ar and PH_3 (0.3%) gas and H_2 gas. The first planar magnetron-deposited films were prepared at a partial pressure of 1.5 mtorr argon or argon plus phosphine while the partial pressure of H_2 was varied from 0.05 mtorr to 0.50 mtorr. The results of room temperature conductivity measurements are shown in Figure 1. The highest conductivity films obtained with PH_3 doping had a room temperature conductivity of 10^{-2} mho/cm . With the addition of 0.5 mtorr H_2 , the room temperature conductivity dropped to $2 \times 10^{-4} \text{ mho/cm}$. This is to be compared with the room temperature conductivity of 10^{-7} mho/cm for the film deposited with the same partial pressures of H_2 and Ar, but no PH_3 . Also shown in the graph are the room temperature conductivity results for films sputtered with 1% diborane (B_2H_6) added to the argon gas. These films also display an increase in conductivity due to the effects of reactive gas doping.

Even though a substantial increase in room temperature conductivity was achieved for films sputtered with Ar +0.3% PH_3 , through-the-film conductivity measurements were limited by contact resistance. With Mo as the contact metal, the contact resistance was greater than 10 ohm-cm^2 . The preliminary cell design calls for contact resistance less than 1 ohm-cm^2 . We believe that the contact resistance is limited by too small a carrier density in the back contact layer. In the next quarter we will pursue a material of higher conductivity using a 3% PH_3 in Ar sputtering gas and optimizing the partial pressures used in film deposition.

Fig. 1 Room-Temperature Conductivity Versus Hydrogen Partial Pressure For Phosphine and Diborane Gas-phase Doping of Hydrogenated Amorphous Silicon

1-2

Section 2

EFFECT OF SUBSTRATE TEMPERATURE AND PARTIAL PRESSURE ON THE
OPTICAL ENERGY GAP

a-Si:H films were deposited in the cylindrical magnetron system during the last contract period as a function of total pressure of Ar, ratio of Ar partial pressure to H₂ partial pressure and temperature of the substrate. The measurement of the optical energy gap, E_{04} , for these films has been completed and the results are presented in Fig. 2.

Several general observations can be made on the basis of the data in Fig. 2. First, E_{04} decreases with increase in substrate temperature for all five combinations of partial pressure. Second, for a given substrate temperature and Ar partial pressure, E_{04} decreased with decrease in the H₂ partial pressure. Third, including a small amount of N₂ increases E_{04} .

2-2

Fig. 2 Energy Gap E_{04} Versus Substrate Temperature For a-Si:H Films
Magnetron-Sputtered at Various Ar/H₂ Partial Pressures

Section 3

EFFECT OF INCORPORATED ARGON IN a-Si:H FILMS

Analysis of bonding structure as a function of incorporation has been performed by IR absorption spectroscopy on a series of films deposited by cylindrical magnetron sputtering at various combinations of Ar and H_2 partial pressures and substrate temperatures. As in planar magnetron sputtering and other deposition methods, there is a relationship between deposition parameters and the resulting i-layer properties for efficient solar cells, i.e., appropriate optical gap, low dark conductivity, high AMI photoconductivity* and "good" SiH/SiH₂ bonding ratios.** To increase our understanding of this parameter space, we have chosen to study the role of included argon in determination of film properties. Ar inclusion occurs in all a-Si:H film deposition methods within the 0 to 5 at.% range. It appears that d.c. magnetron sputtered films are among those containing the least Ar and the highest SiH/SiH₂ bonding ratios.

The results of the study of bonding ratios due to Ar inclusion are presented in Appendix A. The determination of the amount of Ar inclusion is discussed separately in Appendix B. The conclusions of the experiment are that a high percentage of desired SiH bonding is possible in magnetron sputtered films. Further, the formation of (SiH₂)_n appears favored in regions of either high Ar incorporation, energetic particle bombardment, slow deposition rates, or some combination of the above.

*Photoconductivity, a measure of majority carrier transport, is not meant to replace minority carrier lifetime (field modified) as the gauge of i-layer quality. It is, rather, one of the simpler screening parameters. The quality of the i-layer is to be judged by its contribution to the behavior of the actual device.

**Currently it appears that high SiH/SiH₂ bonding ratios are desirable for solar cell quality a-Si:H films.

APPENDIX A

A-1

NOTE: This is a draft of a paper being submitted for publication.

Contents of this paper should not be quoted nor referred to without permission of the authors.

**INFRARED ABSORPTION IN MAGNETRON SPUTTERED a-Si:H FILMS:
EXPERIMENTS USING SHIELDS
TO RESOLVE Si:H_x FORMATION MECHANISMS**

**ARTHUR D. JONATH, JOHN A. THORNTON¹
AND
WILLIAM W. ANDERSON, JOHN L. CROWLEY, HUGH F. MacMILLAN,
AND GERALD B. McCAULEY**

**LOCKHEED PALO ALTO RESEARCH LABORATORY
PALO ALTO, CALIFORNIA 94303 USA**

**¹TELIC CORPORATION
SANTA MONICA, CALIFORNIA 90404 USA**

RESEARCH SUPPORTED BY SERI UNDER CONTRACT NO. XS-0-9237-1

SLIT CAMERA CONFIGURATION USED TO SPUTTER DEPOSIT CATHODE IMAGE

ELECTRON MICROPROBE PROFILES OF a-SI THICKNESS AND ENTRAPPED INERT GAS ACROSS CATHODE IMAGE FILMS

A-5

VARIATION OF a-Si:H INFRARED ABSORBANCE PEAK STRENGTH ACROSS WIDTH OF CYLINDRICAL CATHODE IMAGE

LOCKHEED

VARIATION OF a-Si:H INFRARED ABSORBANCE PEAK STRENGTH ACROSS WIDTH OF CYLINDRICAL CATHODE IMAGE NO. 2

LOCKHEED

VARIATION OF SPECTRAL POSITION OF ABSORPTION PEAKS ACROSS WIDTH OF CYLINDRICAL CATHODE IMAGES

LOCKHEED

EXPERIMENT

- a-Si:H IMAGE OF CYLINDRICAL CATHODE DEPOSITED THROUGH SLIT CAMERA SHIELD (FIG. 1')
- SMALL-ANGLE SCATTERED SPECIES, SUCH AS Ar, ARRIVE AT SUBSTRATE WITH HIGH ENERGIES AND ARE INCORPORATED INTO GROWING FILM AT EDGES OF IMAGE (FIG. 2')
- CENTER OF IMAGE CONTAINS LOWER DENSITY OF SPECIES (FIG. 2)
- TOTAL Ar INCORPORATION < 0.2% (FIG. 2)
- FILM DEPOSITION CONDITIONS:
 - #373 - $P_{Ar} = 3.0 \text{ mtorr}$, $P_{H_2} = 1.5 \text{ mtorr}$, $T_s = 200^\circ\text{C}$
 - #377 - $P_{Ar} = 1.5 \text{ mtorr}$, $P_{H_2} = 0.5 \text{ mtorr}$, $T_s = 200^\circ\text{C}$
- FILM THICKNESS AT CENTER OF IMAGE = $4\mu\text{m}$

RESULTS

- A. ABSORBANCE SPECTRA ACROSS TO CENTER OF IMAGE – SAMPLE #373 (FIG. 3)
- B. LOW SiH_2 RATIO AT CENTER OF IMAGE AS MEASURED BY RATIO OF ABSORBANCE PEAK AT 890 OR 875 cm^{-1} AND THAT OF 2000 cm^{-1} (FIGS. 4 AND 5)
- C. INCREASE IN SiH_2/SiH RATIO AT EDGES OF IMAGE (COMPARE FIGS. 4 AND 5 WITH FIG. 2)
WHERE ENERGETIC Ar INCORPORATION IS IMPORTANT
- D. HIGH-PRESSURE FILM CONTAINS MORE SiH_2 (COMPARE CENTER OF IMAGE REGIONS OF FIGS. 4 AND 5)
THAN DOES LOW-PRESSURE FILM
- E. SPECTRAL POSITIONS OF ABSORPTION LINES CHANGE ACROSS IMAGE (FIG. 6)
- $(\text{SiH}_2)_n$ POLYMER FORM FAVORED OVER SiH_2 AT EDGES OF IMAGE (SHIFT TO 890 FROM 875 cm^{-1})
 - SiH LINE AT 2000 cm^{-1} CHANGES BY +10 OR +15 cm^{-1} ACROSS EDGE OF IMAGE

DISCUSSION AND CONCLUSIONS

- HIGH PERCENTAGE OF DESIRED SiH BONDING POSSIBLE IN MAGNETRON SPUTTERED FILMS (RESULTS A AND B)
- $(\text{SiH}_2)_n$ FORMATION APPEARS FAVORED IN REGIONS OF EITHER HIGH Ar INCORPORATION, ENERGETIC PARTICLE BOMBARDMENT, SLOW DEPOSITION RATES, OR SOME COMBINATION OF THESE (RESULTS C AND E)
- MORE WORK IS NEEDED TO RESOLVE THE FOLLOWING QUESTIONS:
 - IS INCREASED SiH_2 IN HIGH-PRESSURE DEPOSITIONS (RESULTS D AND OTHER²) CONNECTED TO VOID INCREASES ASSOCIATED WITH SUCH FILMS?
 - DOES $(\text{SiH}_2)_n$ POLYMER FORM MORE READILY IN HIGH-PRESSURE FILMS? (COMPARE 875 TO 890 cm^{-2} SHIFT FOR BOTH FILMS IN FIG. 6)
 - IS MAGNITUDE OF 2000 cm^{-1} LINE SPECTRAL CHANGE (RESULT E) ASSOCIATED WITH DENSITY OR STRESS IN FILM?

ACKNOWLEDGMENT

THE AUTHORS WISH TO THANK NAFTALI LUSTIG FOR HELP IN PREPARATION OF THE SAMPLES.

REFERENCES

1. J. A. THORNTON AND D. W. HOFFMAN, "INTERNAL STRESSES IN AMORPHOUS FILMS DEPOSITED BY CYLINDRICAL MAGNETRON SPUTTERING USING Ne, Ar, Kr, Xe, AND Ar + H₂," 27th NATIONAL SYMPOSIUM OF THE AM. VAC. SOC., 13-17 OCT, 1980, DETROIT, MICHIGAN
2. A. JONATH ET AL., UNPUBLISHED DATA

APPENDIX B

B-1

INTERNAL STRESSES IN AMORPHOUS SILICON FILMS DEPOSITED BY
CYLINDRICAL MAGNETRON SPUTTERING USING Ne, Ar, Kr, Xe, and Ar+H₂

John A. Thornton
Telic Corporation
Santa Monica, California 90404

and

David W. Hoffman
Ford Motor Company
Dearborn, Michigan 48121

ABSTRACT

Previous investigations of thin metal films deposited using cylindrical-post magnetron sputtering sources have identified working gas transition pressures below which the internal stresses are compressive and above which they are tensile. The transition pressures increase with the atomic mass of the target material (M_t) relative to that of the working gas (M_g). This paper reports the occurrence of stress transitions in amorphous silicon films formed by dc cylindrical magnetron sputtering from a P-doped Si target using Ne, Ar, Kr, Xe, and Ar+H₂ as working gases. The compressive stresses were comparable to those seen in metal films ($\sim 1 \text{ GN/m}^2$). However, the transition pressures and entrapped gas contents were greater than for metal films with comparable M_t/M_g . Experiments with special shields were conducted to investigate the mechanism of gas entrapment. The occurrence of large compressive stresses and entrapped gas concentrations for films such as these, where $M_t/M_g < 1$, suggests that mechanisms different from simple target ion reflection, proposed in the earlier metallic film studies, are operative.

Paper prepared for presentation at the 27th National Symposium of the American Vacuum Society, October 13-17, 1980, Detroit, MI.

1. INTRODUCTION

In previous studies¹⁻⁶ we have reported measurements of the internal stresses in thin films of various metals deposited at low substrate temperatures (relative to coating material melting point) onto glass wafer substrates surrounding cylindrical-post magnetron⁷ sputtering sources. For each metal/working-gas combination, a transition pressure p_t was identified, below which the coatings were in compression and above which they were unstressed or in tension. The transition pressures were weakly dependent on the source-to-substrate distance and deposition rate, but increased markedly with the ratio of the atomic mass of the coating (target) material M_t to that of the working gas M_g , varying from about 0.3 Pa at $M_t/M_g \sim 0.6$ (Al/Ar, Mo/Xe) to about 2 Pa for $M_t/M_g \sim 5$ (W/Ar, Mo/Ne). Entrapped working gas was found in the high compression coatings. However, the concentrations did not correlate with the stress (or strain) magnitudes. Permutation of the metal/working-gas combinations over common M_t/M_g values yielded common p_t and entrapped gas levels.

It was surmised that the compressive stresses might be caused by the atomic peening action of energetic working gas particles (neutralized and reflected ions) which bombarded the growing coatings and produced an associative, but not causative, entrapment of working gas. Geometric considerations suggested that atom reflection would be particularly important in the post cathode geometry.⁷ Support for this point of view was provided by stress measurements with planar⁸ and hollow⁵ magnetron sources and by special shield

experiments that provided stress and entrapped gas content measurements under fluxes which emanated at normal and oblique angles from post cathodes.^{5,6} Inconsistent with that view, however, has been the observation of large compressive stresses for target/working-gas combinations ($M_t/M_g < 1$) where significant backscattering of gas from the target is not expected.

This paper reports on stress measurements in amorphous Si films (α -Si) formed by cylindrical post magnetron sputtering of Si using Ne, Ar, Kr, and Xe as working gases and in hydrogenated films (α -Si:H) formed by sputtering in Ar+H₂ mixtures. The investigation extends our previous work to an amorphous material and provides more complete data for the range $M_t/M_g < 1$.

2. EXPERIMENTAL PROCEDURE

The coatings were deposited by dc sputtering, using a cylindrical magnetron source which combined an axial magnetic field with magnetic end-confinement.⁷ The target was fabricated from a 0.63 mm diam. by 0.38m long high-purity polycrystalline Si furnace tube, which was neutron-transmutation-doped to a P donor density of $\sim 10^{14}$ cm⁻³. Prior to the deposition of coatings, the chamber was evacuated to a pressure of 0.5 mPa using a Freon-trapped oil diffusion pump. Working pressures were measured with a capacitance manometer.

Stress versus working pressure data for Ne, Ar, Kr, Xe, and Ar+H₂ working gases were obtained by mounting several 18x18x0.15 mm glass wafers surrounding the source at a radius of 0.14m. Discharge current densities were adjusted to provide deposition rates of about 0.3 nm/s and were in the range

16 to 32 A/m². Discharge voltages depended on the gas and working pressure and ranged from 500V (Ne at 1.2 Pa) to 1200V (Xe at 0.13 Pa). Presputtering was done for about 5 min at the desired operating conditions with the substrates shielded. The substrates were then exposed to the sputtered flux for varied times to yield coatings in the thickness range 50 to 300 nm during a given run. The force-per-unit-width in the sputtered films was determined interferometrically by observing the deflection of the glass wafers with reference to an optical flat, as described previously.^{1,5} Thicknesses were measured interferometrically (Tolansky method).

The concentrations of entrapped working gas in the thicker stress samples were determined by electron microprobe analysis, following the procedures outlined in Ref. 5. Working gas entrapment was also investigated, using a shield configuration⁵ which formed a radially resolved image of the cathode, as shown in Fig. 1. Coatings were deposited onto carbon and polished stainless steel substrates, using Ne, Ar, Kr, and Xe at sufficiently low pressures to minimize scattering. Under these conditions the coating at the center of the image was formed and bombarded by Si and by inert gas atoms emanating in directions nearly perpendicular to the target surface, while the coating at the edge of the image was formed and bombarded by species leaving at small angles relative to the target surface. The distribution of entrapped working gas was determined by scanning across the image using an electron microprobe.

3. EXPERIMENTAL RESULTS

Figure 2 shows the force-per-unit-width (integrated stress) versus coat-

ing thickness data for the α -Si films. Film stresses are given by the slopes of the plots. The plots are approximately linear, indicating a near-constant internal incremental stress throughout the coatings. For each gas the low pressure data were found to imply a common average compressive stress with a standard deviation of less than 20% over the thickness range examined.

Figure 3 shows the incremental stress (average slopes in Fig. 2) as a function of the working pressure. Data points which bracket the transition pressures are connected by dashed lines to emphasize the range of uncertainty within which the p_t values are determined. Similar data are shown in Fig. 4 for the α -Si:H coatings deposited at a constant Ar partial pressure and at increasing partial pressures (flow rates) of H_2 , measured before ignition of the discharge. A reduction in compressive stress is seen to have been produced by the H_2 . The fact that the total pressure at the zero-stress point in the Ar- H_2 case shown in Fig. 4 is essentially the same as that for the Ar, Kr, and Xe cases shown in Fig. 3 is coincidental. When an Ar- H_2 partial pressure combination (Ar = 0.20 Pa, H_2 = 0.40 Pa) that yielded low stress was permuted to yield a lower H_2 partial pressure, but a common total pressure (Ar = 0.40 Pa H_2 = 0.20 Pa) and H_2 injection rate (pumping speed increased), high compressive stresses were found in the coatings (triangular data point).

Figure 5 shows the entrapped working gas profiles determined from the shield experiments. The average gas concentrations calculated from these profiles were consistent with the values obtained in the unshielded stress samples deposited at low pressures. The concentrations (atomic percent) in

the stress samples were Ne--3.3%, Ar--0.22%, Kr--0.08%, Xe--0.03%, and Ar-H₂ (0.20 Pa-Ar, 0.27 Pa-H₂) --0.09%. These values are consistent, within a factor of about two, with values estimated from the total sputtered flux and the observed rate of pressure decrease when the magnetron was operated with a fixed charge of gas and with the pumping system valved off. The entrapped gas concentrations decreased with increasing working pressures, as had been observed in the metal coating studies.⁵ A lower Ar concentration was consistently observed in the α -Si:H coatings.

Integration under the Si deposition profile for the Ar case in Fig. 5 shows that about 25% of the material is beyond the projected image size due to vignetting and gas scattering. Gas scattering of 25% of the incident sputtered flux implies that the source-to-substrate distance is about 1/4 of the mean free path at the working pressure (0.13 Pa), and therefore that the scattering cross section is about 6 Å². This is consistent with Ar-Ar cross sections in the energy range of interest for sputtered particles (5-10eV)⁹ and probably not unreasonable for the Ar-Si collisions of interest. Greater scattering (i.e., a more rounded profile) is seen for the Ne case, as would be expected because of the higher working pressures. Thus the Si profiles are consistent with the experimental conditions. The flux directions corresponding to the side-peaks in the noble gas profiles were shown in previous shielding experiments⁶ to indeed produce coatings with high entrapped gas contents and compressive stresses. Therefore, these profiles are not believed to be an experimental artifice, although their occurrence at $M_t/M_g < 1$ is surprising.

4. DISCUSSION

This work has shown that cylindrical magnetron sputtered α -Si and α -Si:H films (like the previously investigated crystalline metal films) are in a state of compression when deposited at low working pressures, and tend to be in a state of slight tension at higher pressures (see Figs. 3 and 4). The magnitudes of the compressive stresses in the α -Si films are comparable to those obtained in refractory metal films (~ 1 to 2 GPa). The compressive stresses were slightly less (~ 0.9 GPa) in the α -Si:H films. (α -Si:H films deposited using the working gas partial pressures that correspond to the high compressive stresses in Fig. 4 have been found to be photoconductive with dark resistivities $\sim 10^8 \Omega\text{-cm}^{10}$, and to contain 5-10 at. % H with a high degree of Si-H bonding.¹¹⁾

The transition pressures and entrapped working gas concentrations for the α -Si films are plotted as a function of M_t/M_g in Fig. 6 and compared with the previous results for metal films. The p_t values for the metal films are seen to show no discontinuity at $M_t/M_g = 1$, even though a simple single-collision model would predict no reflection of the working gas ions at the target for $M_t/M_g < 1$. The entrapped gas concentrations in the metal films are seen, on the other hand, to have decreased, as expected, to below the detectability limit of the microprobe (~ 0.01 at. %) as M_t/M_g approached unity. The α -Si transition pressures are considerably larger than the metal values and are relatively independent of M_t/M_g , at least for $M_t/M_g < 1$. The entrapped working gas content in the α -Si is seen to be more than $\times 10$

larger than that in the metal films, and of considerable magnitude, even for $M_t/M_g < 1$. These observations suggest either that higher energy bombarding species are present, or that the α -Si films are more vulnerable to forming compressive stresses and accumulating entrapped gas than were the metal films.

The relatively high working gas content in the α -Si films is in itself not surprising. The threshold for trapping bombarding Ar has been found to be only ~ 25 eV.¹² Various investigators have found relatively high inert gas contents in sputtered amorphous films of materials like Si,¹³ SiO₂,¹⁴ and GdCo¹⁵ that were subjected to energetic bombardment during deposition. The entrapped gas levels have been attributed,¹⁵ in part, to the fact that amorphous materials are expected to have a high concentration of voids which are larger than the largest interstices (octahedral voids) which are available in close-packed crystalline structures.¹⁶

The question posed by these findings is the origin of the energetic species that produce the stress and gas entrapment for $M_t/M_g < 1$. "The likelihood that we are dealing with an energetic species is suggested, at least in the case of gas entrapment, by the fact that noble gas at thermal energies is not entrapped in evaporated metal films."¹⁷ The gas image results suggest that the energetic particles originate at the cathode or in the plasma. Indeed the existence of transition pressures, and the decrease in entrapped gas content with increasing working pressure, indicate a loss of energy by energetic particles due to gas phase collisions during their passage from the source to the substrates. Other investigators^{18,19} have also seen evidence of

energetic neutral species under conditions where $M_t/M_g < 1$. Explanations such as the sputtering of working gas imbedded in the target²⁰ and backscattering by a multiple-collision process^{18,21} have been suggested. The concentration profiles in Fig. 5, and the continuity of the p_t vs M_t/M_g data in Fig. 6, argue for a common mechanism over a wide range of M_t/M_g including $M_t/M_g < 1$, although the details may differ in the Si case.

Loading of a target with the bombarding ion species, combined with an oblique angle of ion incidence, has been shown to produce energetic ion scattering at small angles relative to the target surface under conditions where $M_t/M_g < 1$.²² Plasma oscillations are known to be present in magnetron discharges.⁷ These oscillations could produce oblique ion incidence, and therefore may be the source of the small angle scattering implied by Fig. 5. The asymmetry of the gas concentration profiles in Fig. 5, and the slight outward displacement of the concentration maxima beyond the shoulders of the Si images, suggest the possibility that some of the energetic species may originate in the plasma surrounding the source. This possibility will be examined in future experiments.

ACKNOWLEDGEMENTS

The authors express their gratitude to Naftali Lustig of Telic and Gerry Grab and Jack Tabock of Ford for their assistance in this work.

REFERENCES

- 1) D.W. Hoffman and J.A. Thornton, Thin Solid Films 40, 355 (1977).
- 2) J.A. Thornton and D.W. Hoffman, J. Vac. Sci. Technol. 14, 164 (1977).
- 3) D.W. Hoffman and J.A. Thornton, Thin Solid Films 45, 387 (1977).
- 4) D.W. Hoffman and J.A. Thornton, J. Vac. Sci. Technol. 16, 134 (1979).
- 5) J.A. Thornton, J. Tabock, and D.W. Hoffman, Thin Solid Films 64, 111 (1979).
- 6) D.W. Hoffman and J.A. Thornton, J. Vac. Sci. Technol. 17, 380 (1980).
- 7) J.A. Thornton and A.S. Penfold, in Thin Film Processes ed. by J.L. Vossen and W. Kern, Academic Press, New York (1978) pp. 75-113.
- 8) D.W. Hoffman and P.J. Goodsmith, SAE Technical Paper Series 790217 (1979).
- 9) R.S. Robinson, J. Vac. Sci. Technol. 16, 185 (1979).
- 10) A.D. Jonath, W.W. Anderson, J.L. Crowley, H.G. MacMillan, F.A. Junga, J.F. Knudsen, K.M. Monahan and J.A. Thornton, Final Report DOE contract 03-79-ET-23040, Lockheed Palo Alto Research Laboratory (March 1980).
- 11) G. Lucovsky, private communication.
- 12) J. Comas and E.A. Wolicki, J. Electrochem. Soc. 117, 1197 (1970).
- 13) M. Wittmer, J. Roth, and J.W. Mayer, J. Electrochem. Soc. 126, 1247 (1979).
- 14) G.C. Schwartz and R.E. Jones, IBM J. Research Dev. 14, 52 (1970).
- 15) J.J. Cuomo and R.J. Gambino, J. Vac. Sci. Technol. 14, 152 (1977).
- 16) D.E. Polk, Acta Metallurgica 20, 485 (1972).
- 17) K.B. Blodgett and T.A. Vanderslice, J. Appl. Phys. 31, 1017 (1960).
- 18) I. Brodie, L.T. Lamont, Jr., and R.L. Jepsen, Phys. Rev. Lett. 21, 1224 (1968).

- 19) W.W.Y. Lee and D. Oblas, J. Appl. Phys. 46, 1728 (1975).
- 20) H.F. Winters and E. Kay, J. Appl. Phys. 38, 3928 (1967).
- 21) C. Brunnée, Z. Physik 147, 161 (1957).
- 22) E. Formann, F.P. Viehböck, and H. Wotke, Canadian J. Phys. 46, 753 (1968).

FIGURE CAPTIONS

- FIG. 1 Special shield configuration used to discern how working gas reflected at various angles from the cathode contributes to the total entrapped gas content in the coatings.
- FIG. 2 Force-per-unit-width (integrated stress) versus film thickness for films sputtered from a Si cylindrical magnetron target in Ne, Ar, Kr, and Xe working gases at indicated pressures and deposition rates.
- FIG. 3 Incremental stress (from Fig. 2) versus working gas pressure for Si films sputtered using a cylindrical magnetron in Ne, Ar, Kr, and Xe.
- FIG. 4 Incremental stress versus total working gas pressure for α -Si:H films sputtered in Ar-H₂ gas mixtures using a cylindrical magnetron. Solid data points correspond to Ar partial pressure of 0.20 Pa with various partial pressures of H₂.
- FIG. 5 Electron microprobe profiles of Si thicknesses and entrapped inert gas concentrations across the width of the cathode images formed using the shield configuration shown in Fig. 1. Working gas pressures: 0.49 Pa for neon, 0.13 Pa for Ar and Kr.
- FIG. 6 Transition pressures (upper curves) and entrapped working gas concentrations (lower curves) for Si, and previously deposited metal films, as a function of the atomic mass ratio of the coating material and working gas.

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6
B-19