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Determination of Argon in Sputtered Silicon Films by Energy-Dispersive X-ray Fluorescence Spectrometry

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Hydrogenated amorphous silicon can be prepared by glow discharge decomposition of silane or by reactive sputtering in an argon + hydrogen plasma. The sputtered films contain some percentage of argon incorporated in them and its role in determining the physical properties of these materials is of interest. This paper describes energy-dispersive X-ray fluorescence (EDXRF) methods which were developed to characterize these kinds of sputtered films. The theoretical principles and the X-ray line intensity correction algorithms for thin-film measurements are reviewed. The advantages of the EDXRF method and the applicability of this technique for other film systems are discussed.

The two basic methods of producing hydrogenated amorphous silicon are the glow discharge decomposition of silane (1) and reactive sputtering in an Ar + H plasma (2). Although both techniques lead to material with good electronic properties (3, 4) the evidence suggests that the two types of films are structurally different. One fundamental difference is that the sputtered films contain some percentage of argon incorporated in them. At this point of our understanding it is not known what role, if any, argon plays in determining the physical properties of the material. It has been suggested, for example, that the argon inhabits voids (5). However, it appears that void formation has not been instigated by the presence of argon but because of structural constraints related to the accommodation of network strain (6). In such a model, considering also the chemical nonreactivity of argon, one may assume that the argon inclusion has no harmful effect on film properties. On the contrary it may have beneficial effects by acting as a steric hindrance against hydrogen diffusion (7). If, however, argon inclusion instigates the void formation in the films, then its presence should always be harmful.

Although the role of argon has been very poorly understood, the amount of argon incorporated into the films can be con-

trolled by varying certain sputtering parameters, for example, the argon partial pressure in the discharge (8), the substrate biasing, the cathode-anode distance, and the substrate temperature. All this has prompted the need to investigate methods for determining the argon content in sputtered amorphous SiH_x thin films. The results can be correlated with the electronic properties of the films in order to define the influence of argon inclusion on film properties.

Energy-dispersive X-ray fluorescence (EDXRF) is well suited for these kinds of thin specimen analyses and it has been widely applied to both thin-film (9-14) and particulate (15-20) systems. In its quantitative application, this technique is rapid, accurate, and nondestructive. The average composition of the film thru a depth of several thousand angstroms (mass per unit area) is determined by comparing the intensities of the characteristic X-ray lines of the film elements to those of suitable standards. The measured Si and Ar X-ray line intensities are corrected for significant background and substrate contribution as well as attenuation by the film prior to use for composition calculations. A secondary target EDXRF system was employed to optimize sensitivity and minimize interferences through judicious choice of excitation conditions. The nearly monoenergetic excitation obtained with this system also provided simplified and accurate algorithms to correct the intensities of measured and exciting X-ray lines for attenuation effects due to the film layer.

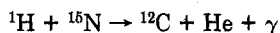
The X-ray fluorescence technique described here is applicable to hydrogenated amorphous silicon films that have been deposited on high-purity quartz (SiO₂) provided the hydrogen content, the film density, and the film thickness are known. The accuracy is limited to that of the calibration standards and is generally $\pm 10\%$ relative for absolute measurements (mass per unit area of Ar and Si) and $\pm 1-5\%$ relative for Ar and Si weight fractions and Ar/Si intensity ratio measurements. This technique may also be extended to different thin film-substrate systems when suitable standards are available for the elements of interest.

EXPERIMENTAL SECTION

The samples were prepared by reactive sputtering of a polycrystalline Si target in a plasma containing argon and hydrogen

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(2). The argon pressure and substrate biasing were changed for some films to determine their effect on the argon content of the films. The hydrogen content of the films was determined independently through the nuclear resonance reaction (21).



The density of one of the films was measured by using a calibrated density gradient setup in a liquid column. The film thickness was measured by studying the transmission spectra of the films, taken with a Cary 17 spectrometer with a 2-mm aperture to eliminate the possibility of a thickness gradient. In the near-infrared region ($\sim 2.0 \mu\text{m}$) the optical density displays oscillations due to coherent multiple reflections across the $\alpha\text{-SiH}_x$ film. The amplitude and the order of these interference fringes were used to calculate the film index of refraction and thickness (22).

A Philips/EDAX EXAM 6 Secondary-Target EDXRF system was used for excitation and measurement of the Si and Ar K α X-ray fluorescent lines of the film samples (film + SiO_2 substrate). This system incorporates a 3000-W tungsten (W) anode X-ray tube as the primary excitation source and six selectable pure element secondary fluorescent targets to provide optimal excitation of sample element X-ray lines between 1.0 and 40 keV. The primary (tungsten) tube was operated at 25 kV and 50 mA with the titanium (Ti) secondary target to excite the Ar and Si K X-ray lines of the film samples. This low primary tube exciting voltage combined with the high current density provided optimal signal-to-background ratios and low backgrounds as well as count rates that did not exceed the linear response range for the X-ray detection system. The sample chamber was flushed with helium during X-ray intensity measurements to minimize absorption by the tube-target-sample-detector path. Detection of Ar and Si K α lines was accomplished with a lithium-drifted silicon (SiLi) detector/preamplifier combined with an EDAX 183A amplifier which incorporates pulse shaping and pulse pileup rejection electronics. An EDAX 711 multichannel analyzer with 800 channels of storage and CRT display were used to present energy spectra of the characteristic lines of the sample. Data processing and instrument control were accomplished with a Data General Nova 3-12 minicomputer interface to a Data General 6030 dual floppy-disk drive.

Similar intensity measurements were made for the sodium (Na), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), and calcium (Ca) K α fluorescent lines of suitable thin-film standards. Thin-film standards were obtained from Micromatter Co., Inc., Seattle, WA, and Columbia Scientific Industries, Inc., Austin, TX.

THEORY

Thin-Film Measurements by X-ray Fluorescence. The total fluorescent intensity for an element in a film of thickness t is given by (9, 10, 12)

$$I_{i,t} = \frac{K(\text{cosec } \Psi_p)I_p^\circ}{\rho[\mu(\lambda_p) \text{ cosec } \Psi_p + \mu(\lambda_i) \text{ cosec } \Psi_i]} [1 - \exp\{-[\mu(\lambda_p) \text{ cosec } \Psi_p + \mu(\lambda_i) \text{ cosec } \Psi_i]\rho t\}] \quad (1)$$

where Ψ_p = the angle between the central ray of the incident primary cone (exciting X-rays) and the film plane, Ψ_i = the takeoff angle between the central ray of the secondary cone (analyte-line) and the film plane, I_p° = the intensity of the incident primary beam, λ_p , λ_i = the primary and analyte-line wavelengths, respectively, $\mu(\lambda_p)$, $\mu(\lambda_i)$ = the mass absorption coefficients of the film for the primary and analyte lines, respectively ($\text{cm}^2 \text{g}^{-1}$); ρ = the density of the film (g cm^{-3}), t = the film thickness (cm), $t \text{ cosec } \Psi_p$, $t \text{ cosec } \Psi_i$ = the path lengths in the film of the primary and secondary beams, respectively, and K = an instrument constant which includes detector efficiency, window absorption, etc.

A. Thin Specimen Criterion. A "thin" specimen may be defined (9, 12, 13) as one for which $m\bar{\mu}_T \leq 0.1$, where m is the mass per unit area (g cm^{-2}) of the analyte line and $\bar{\mu}_T$ is the effective average mass absorption coefficient of the specimen for both the primary and analyte-line X-rays ($\bar{\mu}_T = \mu(\lambda_p) \text{ cosec } \Psi_p + \mu(\lambda_i) \text{ cosec } \Psi_i$). The advantages of ana-

lyzing thin specimens are (1) linear instrument response for analyte-line intensity vs. mass per unit area over several orders of magnitude, (2) minimization of interelement absorption-enhancement effects on measured X-ray intensity, (3) minimization of particle-size effects and simplified corrections when necessary, (4) increased fluorescent-to-background intensity ratio, and (5) low background intensity.

For thin films defined by the criterion above, eq 1 reduces to a simple linear relationship between the fluorescent intensity of the element in the film and the mass per unit area of that element (12)

$$I_i = S_i m_i \quad (2)$$

where I_i = total fluorescent intensity of element i (counts s^{-1}), S_i = sensitivity (counts $\text{s}^{-1}/(\mu\text{g cm}^{-2})$), and m_i = mass per unit area ($\mu\text{g cm}^{-2}$).

B. Analyte Present in the Film and the Substrate. For specimens where the analyte is present in both the film and the substrate, the total measured X-ray line intensity is given by (9)

$$I_i = I_{i,t} + I_{i,\text{sub}} \quad (3)$$

where $I_{i,t}$ is the analyte-line intensity from the film with thickness, t , and $I_{i,\text{sub}}$ is the analyte-line intensity from the element in the substrate after emerging through the overlying film. The value of $I_{i,\text{sub}}$ in eq 3 is not the same as that for a blank substrate because the overlying film attenuates both the primary (exciting) X-rays as well as the substrate secondary X-rays.

The emergent substrate analyte-line intensity, $I_{i,\text{sub}}$, expressed as a function of the blank substrate analyte-line intensity, $I_{i,\text{sub}}^\circ$ is given by

$$I_{i,\text{sub}} = I_{i,\text{sub}}^\circ \exp\{-[\mu(\lambda_p) \text{ cosec } \Psi_p + \mu(\lambda_i) \text{ cosec } \Psi_i]\rho t\} \quad (4)$$

where $I_{i,\text{sub}}^\circ$ is the analyte-line intensity measured for a blank substrate without the overlying film and the other symbols are as defined in eq 1. The analyte line intensity from a pure element film, $I_{i,t}$, may be calculated directly with eq 3 and 4 from constant area intensity measurements for plated and blank specimens. When the film contains more than one element, the density and the mass absorption coefficients for primary and secondary X-rays change with film composition. Therefore, for multicomponent films where one or more analyte elements are also present in the substrate, $I_{i,t}$ cannot be obtained directly and eq 3 and 4 must be solved iteratively using successive approximations to the film composition. The iterations are continued until a self-consistent set of intensity and weight fraction values are obtained which agree to some arbitrarily chosen criterion, say, $\pm 1\%$ relative between iteration steps.

RESULTS AND DISCUSSION

A. Calibration with Thin Film Standards. Thin film standards for Na, Al, Si, P, S, Cl, K, and Ca were obtained as pure elements or pure compounds deposited under vacuum onto nucleopore membrane. Each standard was mounted on a 30-mm plastic X-ray sample cell (film side out) with a $1/4$ -mil polypropylene window stretched across the cell to protect the film. The film standards so mounted were presented to the EDXRF instrument in conventional Philips sample cups with 1-in. circular aperture sample holder inserts to position them over the target-detector region in an inverted geometry (film side down). The incidence and takeoff angles for this system with respect to the sample plane were each 45° . The spinner was used to rotate the sample during the X-ray measurement to obtain average counts over the portion of the film surface seen by the SiLi detector, that is, the central 12 mm diameter of the sample holder inset aperture.

Table I. XRF Intensity and Concentration Data for Amorphous SiH_x Films on High-Purity Quartz^a

sample	film thickness μm	net intens, counts s ⁻¹		mass per unit area, μg cm ⁻²		wt fraction ^b		
		Ar	Si	Ar	Si	H	Ar	Si
Si-213 ^c	2.40	571.5	1674	24.0	429	0.168	0.0441	0.788
					(435)		(0.0436)	(0.788)
Si-182	1.54	329.4	1256	13.8	314		0.0357	0.814
Si-183	1.58	331.1	1267	13.9	325		0.0349	0.815
Si-184	1.58	331.6	1264	13.9	324		0.0350	0.815
Si-189	1.64	330.5	1312	13.9	336		0.0337	0.816
Si-190	1.84	340.5	1460	14.3	374		0.0313	0.819

^a Three sigma detection limits: Si = 0.000 80, Ar = 0.000 10 as weight fractions. Total mass per unit area of the film, m_T (μg cm⁻²) = density (g cm⁻³) × thickness (cm) × 10⁶ (μg g⁻¹). ^b Weight fraction of hydrogen (H) assumed to be 0.15 unless otherwise noted. ^c Measured film density = 2.19 g cm⁻³ for Si-213, density assumed to be 2.2 g cm⁻³ for other films. Si-213 values in parentheses are with the approximation, $m_T = m_{Si}/W_{Si}$, where m_{Si} = silicon mass per unit area and W_{Si} = silicon weight fraction.

Appropriate energy windows in the 0–8 keV energy range were set to monitor the K α lines for Na through Ca. The background regions for these lines and the scattered K α X-radiation from the titanium secondary target were also measured. Standards of 10, 50, and 100 μg/cm² were measured for each element. A blank Nuclepore membrane was also measured. A linear regression model (23) was used to fit the gross intensity and concentration data of the blank and standards for each element. The slope terms from these fits were the respective reciprocal sensitivities (μg cm⁻²/(counts s⁻¹)) for the characteristic K α X-ray line of each element. Background and line overlap contributions to the measured X-ray intensity were corrected by separate terms in the model. Figure 1 shows a plot of the sensitivity (inverse of the slope of the fit in units of counts s⁻¹/(μg cm⁻²)) vs. atomic number for the K α X-ray lines of the standard elements. The solid (lower) line in Figure 1 represents the best fit to the measured data for the standards with 1/4-mil polypropylene windows. The dashed (upper) curve shows the best fit data corrected for the absorption due to the polypropylene window. The sensitivity falls rapidly as the absorption edge of the fluoresced line is displaced lower in energy from the Ti K α exciting energy (i.e., as the atomic number decreases). This is primarily due to the reduction in the mass absorption coefficient of elements with soft X-ray lines for the monoenergetic Ti K α exciting radiation. The Si K α and Ar K α sensitivity factors used to calculate their concentrations in the film samples were taken from the corrected data in Figure 1 (dashed line). Note that though standards for magnesium (Mg) and argon (Ar) were not measured the sensitivities for the K α X-ray lines of these elements could be interpolated from the data in this figure.

B. Sample Analysis. Samples were obtained for analysis as thin films (1.5–2.4 μm) deposited onto 0.5 by 1 in. high-purity quartz plates. A blank quartz plate was also obtained to provide substrate intensity data for the Si K α X-ray line for use in the intensity correction algorithm (eq 4). The film samples were analyzed as received by placing them directly onto the X-ray sample cup inserts (film side down). The back side of each plate (blank SiO₂ without film) and the uncoated quartz plate were also measured to provide duplicate blank values for each film sample. Net intensities for the Ar and Si K α X-ray lines of each sample were obtained by application of a model to correct for background and line overlap contribution to the measured (gross) intensities (23). The net Si intensity from the blank was subtracted from that of the film to obtain the first approximation to the net Si K α intensity from the film.

The mass per unit area for each element was calculated with eq 2 using these intensities and the sensitivity data for Si and Ar K α X-ray lines from Figure 1. For Ar this was the correct

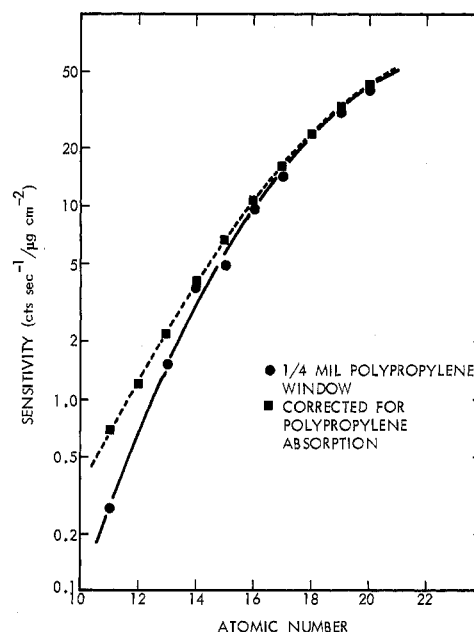


Figure 1. Thin film calibration data, plot of sensitivity (counts s⁻¹/(μg cm⁻²)) vs. atomic number for K α X-ray lines of Na (Z = 11) to Ca (Z = 20).

mass per unit area because the film was thin with respect to Ar K α radiation (by the definition discussed previously) and no Ar was present in the substrate glass. For Si this represented the first approximation to its mass per unit area, m_{Si}^0 , before the Si K α intensity from the blank was corrected for attenuation effects by the overlying film. These initial values were used to calculate the mass per unit area ratio (m_{Si}/m_{Ar}) and weight fractions of Ar and Si in the sample with the equations

$$W_H + W_{Si} + W_{Ar} = 1 \quad (5)$$

$$m_{Si}/m_{Ar} = W_{Si}m_T/W_{Ar}m_T = W_{Si}/W_{Ar}$$

where, W_H , W_{Si} , W_{Ar} = weight fractions of hydrogen, silicon, and argon in the film, respectively, and m_T = total mass per unit area of the film (μg cm⁻²). These values represented the first approximation to the actual weight fractions of Ar and Si in the films. The weight fraction of hydrogen, W_H , was assumed to be 0.15 for the samples where hydrogen content was not measured. The weight fractions determined from eq 5 were used to calculate the mass absorption coefficients of the film for the measured Si K α and the exciting Ti K α X-ray lines ($\mu(\lambda_i)$ and $\mu(\lambda_p)$, respectively) as defined in eq 1. These mass absorption coefficients were then combined with eq 4, the measured film thickness, and the film density (Table I)

to calculate the Si $K\alpha$ intensity from the substrate corrected for the film attenuation. The corrected substrate intensity was subtracted from the total intensity to calculate a new approximation to the net Si $K\alpha$ intensity from the film. This net intensity was used with eq 2 to determine a new approximation to the Si mass per unit area in the film. Equations (5) were then used to generate the second approximations to the weight fractions for Si and Ar in the film. These generally varied significantly from those for the first approximation where the Si $K\alpha$ intensity had not been corrected for the film attenuation. The entire correction process was repeated with the new weight fractions to generate those for the next iteration step and was continued until the weight fractions obtained for Ar and Si agreed with those from the previous iteration to within $\pm 1\%$ relative. Generally only two iterations were required to achieve this agreement.

The net intensity, mass per unit area, and weight fraction data obtained for each sample by this method are listed in Table I. The detection limits expressed as weight fractions were 0.00080 for Si and 0.00010 for Ar. These results were obtained by using the product of measured thickness and measured (or assumed) density, ρt , for the film total mass per unit area in the exponential term of eq 4 as described above. The Si mass per unit area and the Ar and Si weight fractions in parentheses for Si-213 were obtained by a modified calculation scheme. For this approach the film total mass per unit area was computed from the mass per unit area and weight fraction of silicon as defined in eq 5, i.e., $m_T = m_{Si}/W_{Si}$. This value was used for the product, ρt , in eq 4 and represented an independent measure of this product. The results from this calculation agree very well with those using measured density and thickness values for Si-213 (Table I). Also, the total mass per unit area from this method ($552 \mu\text{g cm}^{-2}$) agreed within 5% relative to that calculated from the product of measured density times thickness ($526 \mu\text{g cm}^{-2}$). This excellent agreement is indicative of the overall accuracy of the EDXRF thin film method described here.

CONCLUSIONS

The data presented in Table I show that this EDXRF method is capable of resolving differences of ± 0.0005 weight fraction Ar ($5 \times$ detection limit) and ± 0.004 weight fraction Si of different amorphous SiH_x films which have been sputtered onto high-purity quartz (SiO_2). The accuracy of the technique is dependent upon the accuracy of the thin film standards, the polypropylene window absorption corrections for the standards, the film thickness measurements, the film density measurements, and the mass absorption coefficients used in film attenuation corrections for Si $K\alpha$ intensity. The overall accuracy was about $\pm 10\%$ relative for Ar and Si X-ray line intensity and mass per unit area and about $\pm 1\text{--}5\%$ relative for Si/Ar intensity ratios and Si and Ar weight fractions. The assumed 0.15 weight fraction hydrogen and constant density for some films may have biased their results. Accurate values for these parameters would undoubtedly improve the

accuracy of the results for these films.

The results of Table I suggest that the argon content is comparable to the density deficit of the films. This is consistent with the suggestion that, indeed, the argon inhabits empty spaces in the $\alpha\text{-SiH}_x$ network. Another observation is that the argon content is smaller for films produced at lower argon pressures and on negatively biased substrates (Si-189 and Si-190). Since both of these conditions lead to more argon bombardment of the films, we conclude that the argon content is not related to the arrival rate of argon to the film surface but rather to the available empty spaces in the $\alpha\text{-SiH}_x$ network. Films produced at low argon pressures and negatively biased substrates should be denser and therefore contain less argon.

This technique may also be extended to other multielement film-substrate systems using the calibration data given in Figure 1 for elements between atomic number 11 (Na) and atomic number 20 (Ca). For other elements similar calibration data could also be generated by using appropriate thin film standards.

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