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ELECTROCHEMICAL INSTRUMENTATION

COMPUTER PROGRAMME FOR ELLIPSOMETRIC STUDY OF SURFACE FILMS

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ABSTRACT

Thickness and refractive index of non-light-absorbing surface films can be found out accurately from optical measurements by ellipsometry. However, the mathematical calculations are extremely tedious requiring the use of modern computers. The present paper describes a computer programme developed for this purpose.

Key words: Ellipsometry, Surface film thickness, Computer Programme.

INTRODUCTION

The formation or removal of a film is involved in most of the electrochemical processes. These events are usually of crucial importance in determining the course of the process being studied, and studying them gives us an insight into the nature of the process. The ellipsometer is an experimental tool that allows us to do this with very high accuracy. In ellipsometry, one observes the change in the state of polarization of a polarized beam of light caused by reflection at the specimen surface. From this, one may obtain the thickness and optical constants of the specimen when the specimen is a surface film [1-7]. The ratio of the complex amplitudes of the p and s components (vibrating parallel and perpendicular to the plane of incidence, respectively) of the electric vector $\tilde{E}$ gives the state of polarization $\tilde{\chi}$ Single observation of change in $\tilde{\chi}$ is enough for the determination of two optical constants of a transparent film, (with $k = 0$) say, the thickness and refractive index [8-13]. But, when the film is absorbing, its refractive index becomes complex ($n = n - ik$) and an additional observation is necessary.

THEORY

The reflection coefficients for a film covered surface are given by

$$R^p = \frac{r_{12}^p + r_{23}^p e^{iD}}{1 + r_{12}^p r_{23}^p e^{iD}} \qquad \ldots (1)$$

$$R^s = \frac{r_{12}^s + r_{23}^s e^{iD}}{1 + r_{12}^s r_{23}^s e^{iD}} \qquad \ldots (2)$$

where the superscripts p and s denote the components of light parallel and perpendicular to the plane of incidence, respectively.

The reflection coefficients for the boundary between i^th^ and j^th^ medium, r_{ij}^p and r_{ij}^s, are given by the equations,

$$r_{ij}^p = \frac{n_i \cos \phi_j - n_j \cos \phi_i}{n_i \cos \phi_j + n_j \cos \phi_i} \qquad \ldots (3)$$

$$r_{ij}^s = \frac{n_i \cos \phi_i - n_j \cos \phi_j}{n_i \cos \phi_i + n_j \cos \phi_j} \qquad \ldots (3)$$

where n_i and ϕ_i are the refractive index of the ith medium and an angle of incidence in that medium respectively; i is 1, 2 and 3 for the ambient medium (air or solution), the film and the substrate underneath, respectively. n_i and ϕ_i are in general, complex members.

D is related to the thickness of the film D_2 and wavelength λ as

$$D = -4 \pi D_2 n_2 \cos \phi_2 / \lambda \qquad \ldots (5)$$

$$\tilde{n}_2 = n - ik \qquad \ldots (6)$$

Thus R^p and R^s are complex functions of the three unknown quantities of the film n, k and D_2 and other variables in the expressions λ, ϕ_1, n_1 and n_3 are all known or measurable.

In order to determine the film constants, two parameters Δ and ψ are measured by ellipsometry. These are related to R^p and R^s as follows:

$$\tan \psi \, e^{i\Delta} = \frac{R^p}{R^s} \qquad \ldots (7)$$

Equation (7) is, in fact, two equations because both sides have complex members. We can write [14]

$$\tan \psi \, e^{i\Delta} = F(n, k, D_2 \ldots) \exp [iG(n, K, D_2 \ldots)] \qquad \ldots (8)$$

$$\tan \psi = F(n, k, D_2 \ldots) \qquad \ldots (9)$$

$$\Delta = G(n, k, D_2 \ldots) \qquad \ldots (10)$$

RESULTS AND DISCUSSION

The above two equations are extremely complicated and their solution and use for interpreting ellipsometric data requires electronic computation. Iteration technique is generally adopted. For each value of refractive index of the film, various values of Δ and ψ parameters are generated varying the thickness of the film. Computer programme has been written for generating tables of Δ, ψ and thickness.

The optical constants of transparent films can be found out by using the experimentally determined Δ and ψ values in the above tables. The programme given below is for finding the thickness and refractive index of silicon dioxide film on silicon substrate. The programme is suitable for nonabsorbing films, and is designed for use with a microcomputer with lesser memory capacity also. Test runs have been made in AL 2000 computer. Results have been cross checked and found to be accurate up to 2nd decimal place (as evident from Table I) with literature values [15].

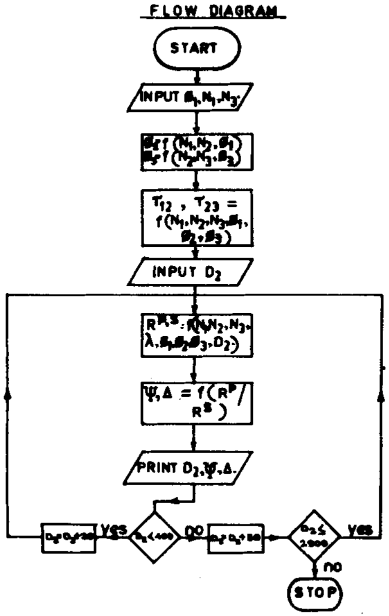
```
C      GENERATION OF THICKNESS
          DELTA AND PSI TABLES
10     REAL N1,N2
20     PHI1=1.2217
30     N1=1.0
       X1=0.0
       DO 690 I=1,3
       X1=X1+0 05
       N2=1.40+X1
       WRITE(2 51)
       WRITE(2 51)
 51    FORMAT(1X)
       WRITE(2,55) N2
 55    FORMAT(40X,5HN2=   ,F4.2)
       WRITE(2,51)
       WRITE(2,51)
 50    A=N1*SIN(PHI1)/N2
 60    C=COS(PHI1)
 70    B=SQRT(1-A*A)
 80    R12P=(N1*B-N2*C)/(N1*B+N2*C)
 90    R125=(N1*C-N2*B)/(N1*C+N2*B)
 100   E=4.07
 110   D=0.033
 120   F=N2*A*E/(E*E+D*D)
 130   G=N2*A*D/(E*E+D*D)
 140   P=SQRT((1-F*F)*(1+G*G))
 150   Q=-F*G
 160   DR1=(N2*P+E*B)**2+(N2*Q-D*B)**2
 170   R1NR=(N2*P)**2-(E*B)**2+
           (N2*Q)**2-(D*B)**2
 180   R2NR=(N2*B*(D*P+E*Q))*2
 190   X=E*P+D*Q
 200   Y=D*P-E*Q
 210   DR2=(N2*B+X)**2+Y**2
 220   R3NR=(N2*B)**2-X*X-Y*Y
 230   R4NR=2*Y*N2*B
 240   A1=R1NR/DR1
 250   A2=R2NR/DR1
 260   A3=R3NR/DR2
 270   A4=R4NR/DR2
 280   A00=SQRT((N2**2-SIN(PHI1)**2))/5461
       K1=0
       DO 690 K=1,21
       K1=K1+1
       D2=20*(K1-1)
       IF (K1 LT 21) GOTO 300
       IF (K1 EQ 21) GOTO 281
 281   CONTINUE
       DO 325 L=1,50
       D2=400 0+(L*50)
 300   CONTINUE
 290    RDELTA=44*D2*A00/7
        RRDEL=RDELTA*180*7/22
 310    EDR=COS(2*RDELTA)
        EDI=-SIN(RDELTA*2)
        A5=A1*EDR-A2*EDI
       A6=A2*EDR+A1*EDI
        A7=R12P+A5
        A8=1+R12P*A5
        A9=R12P*A6
        A10=A8**2+A9**2
       A11=A7*A8+A6*A9
       A12=A6*A8-A7*A9
       RPR=A11/A10
       RPI=A12/A10
       A13=A3*EDR-A4*EDI
       A14=A4*EDR+A3*EDI
       A15=R125+A13
       A16=1+R125*A13
       A17=R125*A14
       A18=A16**2+A17**2
       A19=A15*A16+A14*A17
       A20=A14*A16-A15*A17
       RSR=A19/A18
       RSI=A20/A18
       A21=RPR*RSR+RPI*RSI
       A22=RPI*RSR-RPR*RSI
       A23=RSR**2+RSI**2
       ROAR=A21/A23
       ROAI=A22/A23
       AA=-ROAR
       BB=-ROAI
       PSI=ATAN(SQRT(AA**2+BB**2))*180*7/22
       IF (AA) 400,425,450
400    AA=-AA
       IF (BB) 475,480,525
475    BB=-BB
       DELTA=ATAN(BB/AA)
       DELTA=DELTA*180*7/22
       DELTA=DELTA+180
       GOTO 600
480    DELTA=180
       GOTO 600
525    DELTA=ATAN(BB/AA)
       DELTA=DELTA*180*7/22
       DELTA=180-DELTA
       GOTO 600
425    CONTINUE
       IF (BB) 550,700,575
550    DELTA=270
       GOTO 600
575    DELTA=90
       GOTO 600
450    CONTINUE
       IF (BB) 580,585,590
580    BB=-BB
       DELTA=ATAN(BB/AA)
       DELTA=DELTA*180*7/22
       DELTA=360-DELTA
       GOTO 600
585    DELTA=0
       GOTO 600
590     DELTA=ATAN(BB/AA)
         DELTA=DELTA*180*7/22
                GOTO 600
600     CONTINUE
        WRITE(2,650) D2,PSI,DELTA
650     FORMAT(8X,F5.0,2(10X,F9.4))
690    CONTINUE
700    END
```

Table 1: PSI and DELTA values generated for various film thicknesses

$N_2 = 1.5$

D_2 Å	PSI	PSI [15]	DELTA	DELTA [15]
20	11.961	11.965	172.522	172.522
40	12.117	12.120	166.260	166.260
60	12.360	12.354	160.180	160.180
80	12.685	12.689	154.345	154.343
100	13.084	13.087	148.797	148.795
200	15.885	15.888	125.817	125.809
500	26.691	26.695	89.604	89.653
1000	58.358	58.324	81.096	81.114
1500	41.634	41.691	281.675	281.646
2000	20.398	20.436	253.832	253.865
2500	14.802	14.777	132.854	133.053

This programme has been extended to accommodate absorbing films also. It requires a computer which has a facility to handle complex numbers as such. The advanced programme has also been tested in IBM 370/155 system for iron oxide films on iron substrates.



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