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ELECTROCHEMICAL INSTRUMENTATION

COMPUTER PROGRAM FOR THE STUDY OF LIGHT ABSORBING SURFACE FILMS BY ELLIPSOMETRY

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A computer program for finding out the thickness, refractive index and extinction coefficient of opaque surface films from the experimental observation of angle parameters psi and delta has been formulated. This program with suitable modification can be applied to the optical constant determination of transparent films also.

Key Words: Ellipsometry, film thickness, refractive index, extinction coefficient, computer program

INTRODUCTION

Evaluation of the nature, composition and amount of surface film formed over metallic substrates is of paramount importance in understanding the kinetics, mechanism and type of film formation encountered in electrochemical processes. Ellipsometry is a very useful and accurate technique providing almost all the relevant information necessary in such studies both qualitatively and quantitatively [1 - 8]. Ellipsometry can very easily distinguish an oxide film from an adsorbed film [9]. Similarly, monitoring of psi and delta experimental parameters provides data about kinetics of film growth as well as dissolution. Accurate film thickness and optical constants like refractive index and extinction coefficient of surface films can be determined from ellipsometry. However, since the calculation involves large number of reflection coefficients, computation becomes time consuming and tedious. Hence the need for a computer for calculations. Computer program developed for non-light-absorbing transparent surface films is reported earlier [10].

The present work is the development of a more general computer program useful for all types of films, light absorbing and non-absorbing. The case of absorbing films is complicated because of the complex nature of the refractive index value for the surface film that has to be used in the calculation. The extinction coefficient K_2 which is zero in the case of non-absorbing films assumes a definite value when the film absorbs light. The absorption of light characterised by the K_2 factor cannot be neglected in the study of absorbing films. Most of the surface films are light absorbing exception being films formed by valve metals such as Ta, Nb, Al and Ti which are optically transparent with K_2 equal to zero. Therefore, there is a compelling need for a computer program to evaluate the optical constants and thickness of opaque films.

THEORY AND COMPUTATION

Opaque films have refractive index of the form X + iY, real part denoting the conventional refractive index and the imaginary part representing the extinction coefficient. As the generally available microcomputers cannot handle complex numbers, they are separated into real and imaginary parts and proceeded independently collecting all the real and imaginary portions in each relation. Relevant theory behind all the calculations is already reported [10].

When the surface film is absorbing type, the angles subtended by the light beam within the film and substrate medium, namely, Phi_2 and Phi_3 respectively, become complex. The cosine of such angles needed for finding out the reflection coefficients at the air-film interface and film-substrate interface also assume complex structure with real and imaginary parts. Further both the real and imaginary parts involve hyperbolic functions of the type Cosh and Sinh of angle. One small approximation made in the formulation of previous computer program for the calculation of cosine terms is also removed in the present work to give a more general and vigorous software for absorbing film analysis. Flow diagram describing the procedure adopted in formulating the program is almost similar to the one already reported [10].

Computing system used is an Apple IIe compatible 8-bit microcomputer based on 6502-A microprocessor. Language chosen for writing the program is MBASIC as it is capable of accommodating six character variables necessary for representing the large number of variables involved. The developed program is listed at the end of this paper.

RESULTS AND DISCUSSION

Table below presents the various computer generated values of psi and delta angles for different thicknesses of the surface film, silicon dioxide film over silicon.

Table I :psi and delta values generated for various thickness values of silicon dioxide film of refractive index = 2.2 - 0.22 i

TH A°	psi	psi [1]	delta	delta [1]
0	13.7	12.5	152.9	158.0
150	21.5	18.0	118.9	128.0
300	25.6	22.0	93.5	92.0
450	29.6	27.0	61.0	65.0
600	36.2	33.0	24.0	30.0
900	30.3	21.0	317.0	330.0
1050	20.0	15.0	294.0	298.0
1200	9.0	6.0	250.0	265.0
2000	20.0	15.0	360.0	12.0

```
10 REM OPTICAL CONST.-ABSORBING FILM
20 N1=1:R2=2.2:K2=.22:PHI1=1.2217:
30 Q1=COS(PHI1):T12=R2*R2+K2*K2
40 T1=N1*SIN(PHI1)*R2/T12
50 T2=N1*SIN(PHI1)*K2/T12
60 T8=1+F*F+G*G
70 T9=SQR(T8*T8-4*F*F)
80 COSHB=SQR(.5*(T8+T9))
90 SINA=SQR(.5*(T8-T9))
100 SINHB=SQR((COSHB)^2-1)
110 COSA=SQR(1-SINA*SINA)
120 Q2=COSA*COSHB
130 Q3=-SINA*SINHB
140 R3=4.05:K3=.028
150 T34=R3*R3+K3*K3
160 RKT1=R2*T1-K2*T2
170 RKT2=K2*T1+R2*T2
180 T3=(RKT1*R3-RKT2*K3)/T34
190 T4=(RKT1*K3+RKT2*R3)/T34
200 T20=1+T3*T3+T4*T4
210 T21=SQR(T20*T20-4*T3*T3)
220 COSHB=SQR(.5*(T20+T21))
230 SINA=SQR(.5*(T20-T21))
240 SINHB=SQR((COSHB)^2-1)
250 COSA=SQR(1-SINA*SINA)
260 Q4=COSA*COSHB
270 Q5=-SINA*SINHB
280 RK=R2*R2+K2*K2
290 PR12RN=N1*N1*(Q2*Q2+Q3*Q3)-Q1*Q1*RK
300 PR12IN=2*N1*K2*Q1*Q2+2*N1*R2*Q1*Q3
310 PR12D=(N1*Q2+R2*Q1)^2+(N1*Q3-K2*Q1)^2
320 PR12R=PR12RN/PR12D
330 PR12I=PR12IN/PR12D
340 Y1=R2*Q2+K2*Q3
350 Y2=K2*Q2-R2*Q3
360 SR12RN=N1*Q1*Q1-Y1*Y1+Y2*Y2
370 SR12IN=2*N1*Q1*Y2
380 SR12D=(N1*Q1+Y1)^2+Y2*Y2
390 SR12R=SR12RN/SR12D
400 SR12I=SR12IN/SR12D
410 Y3=R2*Q4+K2*Q5
420 Y4=R3*Q2+K3*Q3
430 Y5=K2*Q4-R2*Q5
440 Y6=K3*Q2-R3*Q3
450 PR23RN=Y3*Y3-Y4*Y4-Y5*Y5+Y6*Y6
460 PR23IN=2*Y3*Y6-2*Y4*Y5
470 PR23D=(Y3+Y4)^2+(Y5+Y6)^2
480 PR23R=PR23RN/PR23D
490 PR23I=PR23IN/PR23D
500 Y7=R2*Q2+K2*Q3
510 Y8=R3*Q4+K3*Q5
520 Y9=R2*Q3-K2*Q2
530 Y10=R3*Q5-K3*Q4
540 SR23RN=Y7*Y7-Y8*Y8-Y9*Y9+Y10*Y10
550 SR23IN=2*Y7*Y10-2*Y8*Y9
560 SR23D=(Y7+Y8)^2+(Y9+Y10)^2
570 SR23R=SR23RN/SR23D
580 SR23I=SR23IN/SR23D
590 DPART=SQR(RK-N1*N1*SIN(PHI1)^2)/5461
600 FOR K1=1 TO 72
610 IF K1<22 THEN 630
620 IF K1=>22 THEN 640
630 TH=20*(K1-1):GOTO 650
640 K=K1-21:TH=400+(K*100)
650 D=2*44*TH*DPART/7
660 Y15=PR23R*COS(D)+PR23I*SIN(D)
670 Y16=PR23R*SIN(D)+PR23I*COS(D)
680 Y17=(1+PR12R*Y15+PR12I*Y16)
690 Y18=PR12I*Y15-PR12R*Y16
700 Y19=PR12R+Y15
710 Y20=PR12I-Y16
720 Y178=Y17*Y17+Y18*Y18
730 RPR=(Y19*Y17+Y20*Y18)/Y178
740 RPI=(Y20*Y17-Y19*Y18)/Y178
750 Y21=SR23R*COS(D)+SR23I*SIN(D)
760 Y22=SR23R*SIN(D)-SR23I*COS(D)
770 Y23=1+SR12R*Y21+SR12I*Y22
780 Y24=SR12I*Y21-SR12R*Y22
790 Y25=SR12R+Y21
800 Y26=SR12I-Y22
810 Y234=Y23*Y23+Y24*Y24
820 RSR=(Y25*Y23+Y26*Y24)/Y234
830 RSI=(Y26*Y23-Y25*Y24)/Y234
840 ROWD=RSR*RSR+RSI*RSI
850 ROWR=(RPR*RSR+RPI*RSI)/ROWD
860 ROWI=(RPI*RSR-RPR*RSI)/ROWD
870 AA=-ROWR:BB=-ROWI
880 PSI=ATN(SQR(AA*AA+BB*BB))*57.2
890 IF AA<0 THEN 920
900 IF AA=0 THEN 1060
910 IF AA>0 THEN 1110
920 AA=-AA
930 IF BB<0 THEN 960
940 IF BB=0 THEN 870
950 IF BB>0 THEN 1020
960 BB=-BB
970 DELTA=ATN(BB/AA)
980 DELTA=DELTA*57.27
990 DELTA=DELTA+180
1000 GOTO 1230:DELTA 180
1010 GOTO 1230
1020 DELTA=ATN(BB/AA)
1030 DELTA=DELTA*57.27
1040 DELTA=180-DELTA
1050 GOTO 1230
1060 IF BB<0 THEN 1090
1070 IF BB=0 THEN 1250
1080 IF BB>0 THEN 1100
1090 DELTA=270:GOTO 1230
1100 DELTA=90:GOTO 1230
1110 IF BB<0 THEN 1140
1120 IF BB=0 THEN 1080
1130 IF BB>0 THEN 1200
1140 BB=-BB
1150 DELTA=ATN(BB/AA)
1160 DELTA=DELTA*57.27
1170 DELTA=360-DELTA
1180 GOTO 1230:DELTA=0
1190 GOTO 1230
1200 DELTA=ATN(BB/AA)
1210 DELTA=DELTA*57.27
1220 GOTO 1230
1230 LPRINT TH,PSI,DELTA
1240 NEXT K1
1250 END
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The fixed constants used in the study are: angle of incidence 70°, wavelength 5461 A° and the complex index of refraction of silicon, 4.050- 0.028i. The complex refractive index of the film assumed is 2.2 - 0.22i. Literature values [1] are found to be fairly agreeing with the psi and delta values obtained in the work thereby proving the correctness of the software. The psi and delta values especially for absorbing films are not readily available in the literature. They are computed from the psi versus delta graphs for different thickness values reported in the manual on ellipsometry [1] for silicon dioxide. Hence they are only approximate. Nevertheless, it is obvious from the Table that both psi and delta parameters obtained in the present work show the same trend in variation as the corresponding angles of the reference. For a thickness variation in the range 0-2000 A°, the psi values exhibit an increasing tendency whereas the delta values showing the reverse. Majority of the ellipsometric studies are qualitative, interested mainly in getting an idea about the type of film formed, whether adsorbed or oxide film and/or the formation or dissolution of surface films. Sometimes even the kinetics studies for formulating rate constants can be planned in a qualitative manner. It is clearly evident from the above discussion that for most of the ellipsometric work an idea about the trend in angular variation is much more important rather than the actual values of psi and delta. Hence, the present computer program providing that vital information about angular variation is in excellent agreement with the literature and serves the purpose very well.

One advantage of this program is its generality i.e. it can be used for both transparent and opaque surface films. When the program is applied to the transparent films, only the K_2 value appearing in the first statement has to be put zero. Rest of the program can be the same.

In conclusion, it can be stated that the present program is capable of finding out the thickness and optical constants of both absorbing and non- absorbing films.

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