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Ellipsometry Study on Nanoparticles Grown by Atomic Layer Deposition

Xueqi Zhou[2],Ying Zhang[2], Zhengqiong Dong[1,3], Shiyuan Liu[1,3], Chuanwei Zhang[1],Bin Huang[2], Kun Cao[2], Bin Shan[2], Rong Chen[1*]
[1]State Key Laboratory of Digital Manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.
[2]State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering ,Huazhong University of Science and Technology, Wuhan 430074, China.
[3] Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China.
*Corresponding author: rongchen@mail.hust.edu.cn

ABSTRACT

Spectroscopic Ellipsometry (SE) was chosen to study thin film growth in atomic layer deposition (ALD). It was shown that Cauchy model had limitations in predicting the ultrathin film thickness at initial few deposition cycles, and the fitting results depend on wavelengths range greatly. Effective Medium Approximation (EMA) model is capable of predicting ultrathin film's physical properties. Our experiments on Al_2O_3 growth give supporting evidence on the applicability of EMA model, where it is used to successfully explain the initial nucleation and island like growth. EMA model can be extended to be used for Palladium thin film, which can give reasonable thickness and void content.

INTRODUCTION

As the length scale of devices keeps shrinking, the critical layer thicknesses are steadily decreasing for large scale integrated circuits. Atomic layer deposition (ALD) is a potential method for depositing ultrathin, uniform films with atomic control of the thickness [1-3].It mainly consists of two self-limiting reactions on surface, repeated in alternating ABAB…sequences. These half reactions can avoid chemical vapor deposition during the film growth process. The self-limiting nature of ALD growth process brings several advantages: precise and feasible control of thickness at the level of angstrom or monolayer, capable of fabricating conformal, continuous and pinhole-free films on high aspect ratio structures[4,5].

The development of an accurate characterization technique to determine thin films' thickness during ALD process is of great importance to ultrathin film fabrication technology. Among nano metrology tools, spectroscopic ellipsometer (SE) is known as a sensitive, accurate, and non-destructive thin film characterization technique[6-8]. The thickness of thin film can be determined by detecting the change of the light polarization after the incident light reflects from or transmits through the substrate surface. The polarization is described by an amplitude ratio ($\tan\Psi$) and phase difference (Δ) of p-light and s-light, as in equation (1):

$$\rho=\tan(\Psi)\, e^{i\Delta}=R_p/R_s \qquad (1)$$

R_p and R_s represent the complex Fresnel coefficients of p-light and s-light polarizations respectively.SE is sensitive to sub-monolayer surface coverage, giving optical constant and thickness measurements simultaneously. In recent years, SE technique has been extended to in-situ thin film characterization due to its accuracy, mild testing conditions and simplicity of operation. It is now playing a more and more important role in in-situ characterization of ALD process [9].

To get film thicknesses and optical constants from the SE measurement data, a model-based analysis must be performed. Usually a layered optical model is used to represent the actual structure of the sample. Among all the models in SE data analysis, Cauchy model is a widely used one for transparent or semi-transparent thin film thickness analysis. It's a dispersion layer and on different parts over the spectral range, the optical constants are expressed as a complex refractive index, as in equation (2). The optical constants can be represented by an index which varies slowly as a function of wavelength, as in equation (3); and an exponential Urbach absorption tail, as in equation (4).

$$\tilde{n}= n + ik \quad (2)$$

$$n(\lambda)=A+B/\lambda^2 +C/\lambda^4 \quad (3)$$

$$k=kamp*e^{(E-Bandedge)} \quad (4)$$

Cauchy model treats the film as an ideal smooth film and shows great accuracy for thin films above 3nm, which has been calibrated by TEM in many reports [10]. But it fails to meet the challenge requirement of measuring ultrathin films. In general, thin film has three growth modes: Island growth (Volmer-Weber), Layer by layer growth (Frank-van der Merwe) and Mixed growth (Stranski-Krastanov).For ultrathin film system, early growth stage has made up a large proportion and differs a lot from the stable growth period[11,12], which renders the Cauchy model inappropriate in many cases. Effective Medium Approximation (EMA) model describes the macroscopic properties of a material based on the properties and the relative fractions of its components. It's frequently used for getting information about a mixed film layer in thin film characterization [13,14].Maxwell-Garnett EMA is chosen in our date analysis, which assumes that spherical inclusions of materials exist in a host matrix of material. In our system, Al_2O_3 （Palladium） has the biggest fraction and void content is significantly less than it, thus we treat Al_2O_3 （Palladium） as the host.

We report here the use of Maxwell-Garnett EMA model to deal with such non-ideal ultrathin films grown by ALD. We compare the Cauchy and EMA model in SE characterization of Al_2O_3 and find the EMA model better in fitting the thickness and refractive index for ultrathin film. Further study reveals that EMA model can be applied to Pd thin film as well.

EXPERIMENT

Thin film fabrication

Al_2O_3 films were grown using $Al(CH_3)_3$ [trimethylaluminum (TMA)] (Nanjing university MO source, 99.99%) and deionized water (Millipore, resistivity=18.2 MΩ•cm @ 25℃). The carrier gas was high-purity nitrogen (99.999%). The experiment was carried out in Picosun Sunale R-200. The reactor chamber pressure was kept at 600Pa and the deposition temperature was maintained at 300℃. Two precursors' bottles were kept at room temperature.

Palladium films were grown by using Pd(II) hexafluoroacetylacetonate ($Pd(hfac)_2$, Sigma-Aldrich, 97%) and formalin (37% formaldehyde in water with 15% methanol as stabilizer) as precursors. The films were grown in a bottom heated reactor system at 200 ℃ for reaction. The reaction pressure maintained at 70Pa with nitrogen (99.999%) gas continuously passing through the chamber at 100sccm. The $Pd(hfac)_2$ was sealed in a stainless steel bottle heated to 60℃. Formalin was kept at room temperature. All the lines were kept at 100℃ to avoid condensation.

SE Characterization

Films' thicknesses and optical constant were measured using a J. A. Woollam variable-angle spectroscopic ellipsometer (RC2). Measurement was taken at an incidence angle of 65°.

DISCUSSION

Al_2O_3 thin film analysis

We have used two models (Cauchy and EMA model) to characterize Al_2O_3 films. Fig.1 gives the calculated film thickness and refractive index.

The liner growth rate per cycle (GPC) of two models show no appreciable differences, and GPC is about 0.90±0.02 Å/cycle, as is shown in Fig.1(a). The GPC is similar to previous literature results.

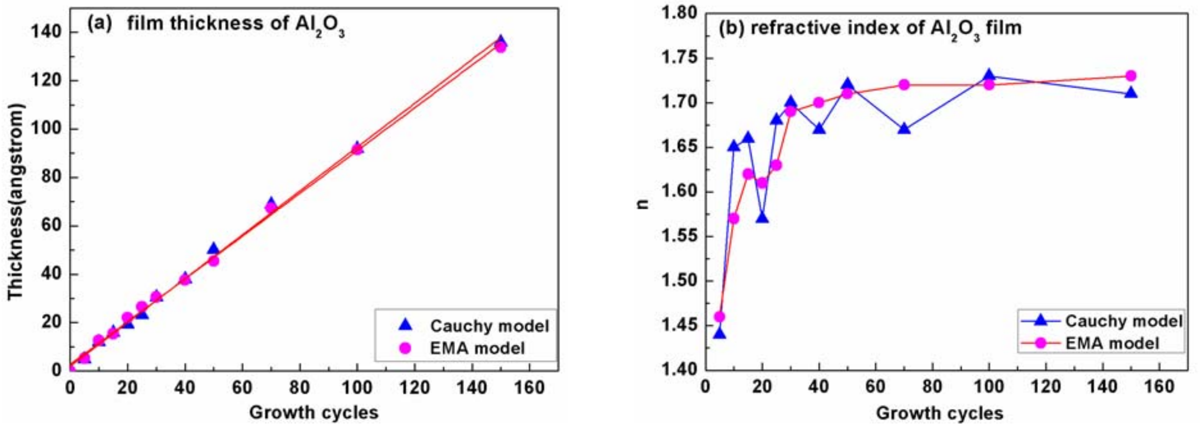

Fig. 1 (a) calculated thin film's thickness (b) calculated refractive index (n)

The optical constant from both Cauchy model and EMA model are shown in Fig 1(b). We can get much useful information from this figure: firstly, n increases with thickness, and increases faster in small thickness region, while after reaching some thickness, it increases asymptotically to a saturated value. Secondly, both of their saturated n are about 1.72-1.73 at 632.8nm wavelength, the value is reasonable and are in general agreement with other people's work[15,16]. Thirdly, for thin films of small cycles, the growth is not stable, which is reflected by the fluctuation of optical constant. This phenomenon is a result of the early nucleation process, and the film is usually not a smooth surface as show in Fig.2.

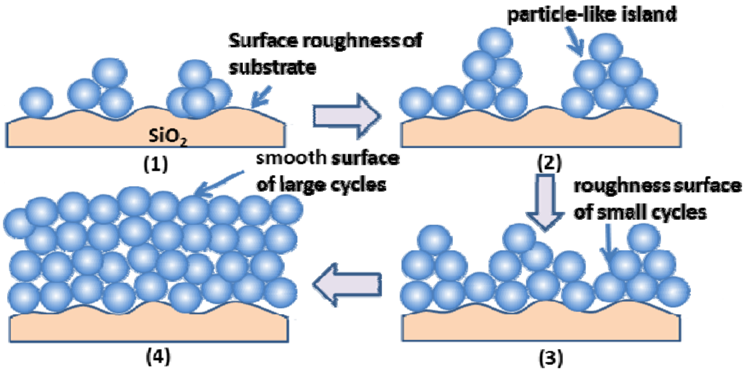

Fig. 2 Schematic diagram of the growth mechanism of ALD

Fig.2 is a schematic diagram of the nucleation process of ALD film growth process. At initial few cycles, the surface and interface roughness are large, especially if the growth is of the island-growth mode; as growth continues, the films become thicker, the surfaces become smoother. So the measurement is largely influenced by the surface and interface situations of ultrathin films. From the analyses above, we know that the initial stage has a great impact on the optical constant. If done without concentration, the Cauchy model can yield unrealistic results. In our fitting, we have determined some fitting tips for the Cauchy model. Cauchy model is most suitable for transparent film measurements, but has some limits in fitting a large wavelengths range. In our fitting, the 5-25 cycles results are fitted using 380-800 nm wavelengths range; 30-70 cycles results are fitted with 240-800 nm wavelengths range; >70 cycles results are fitted with 200-800 nm wavelengths range. In the Cauchy model, while fitting to larger wavelengths range may yield more precise results for smooth films, it will lead to unphysical results if the same range of fitting is directly applied to a non-ideal thin film, like 20 cycles. This reflects the strong relationship between n and fitting wavelengths range. If the fitting target is a non-ideal ultrathin film with complicated surface structure with void defects and surface roughness, Cauchy model which intrinsically treats it as a homogeneous ideal smooth film will lead to large errors, especially when in the ultraviolet band, the interaction between light and ultrathin film are much more complicated, we usually can’t fit the complex trend of measured parameters well in this band or just get a feasible mathematical fitting without any physical meaning. When at longer wavelengths, n just decided by equation (2), the measured parameters trends are much simple for thin film. While for thick film, it’s more like an ideal film, so large wavelengths range fitting is suitable.

For EMA model, the optical constant of Al_2O_3 is automatically calculated in Maxwell-Garnett EMA model by equation (5).

$$(\varepsilon-\varepsilon_A)/(\varepsilon+2\varepsilon_A)=f_B\,(\varepsilon_B-\varepsilon_A)/(\varepsilon_B+2\varepsilon_A)+f_C\,(\varepsilon_C-\varepsilon_A)/(\varepsilon_C+2\varepsilon_A) \tag{5}$$

A refers to the host material and $f_{B(C)}$ is the volume fractions of the constituent materials, with dielectric functions ε_A, ε_B, ε_C, here fc is set to zero. With EMA model, we can get physical results fitting to all the wavelength range, indicating that the EMA model is more realistic. It also saves our efforts in finding the wavelengths range of fitting. The Al_2O_3 EMA results were all fitted at 200-800nm wavelengths. As shown in Fig.1(b), EMA model shows less fluctuation than that of Cauchy model, which shows its priority as well.

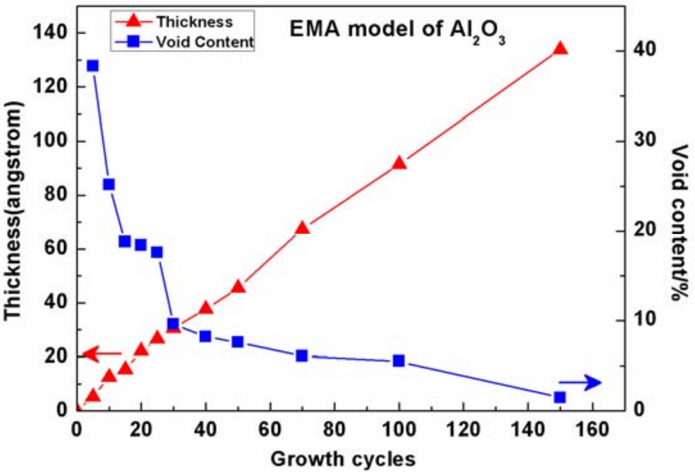

Fig. 3 Void content of different thickness Al_2O_3

Moreover, the EMA model can provide us the void percentage. Fig.3 shows that void content reduces with the increase of film thickness. When the thickness is large enough, the void percentage reduces to as low as 1%, indicating that the thin film surface is smooth. This is in agreement with the ALD thin film growth process.

Pd thin film analysis

During the ALD process, because the interactions between the Pd atoms are stronger than those between the Pd atom and SiO_2 substrate, Pd has the tendency to form nanoparticles [11,12,17,18]. This so called Volmer-Weber (island) growth, which has brought surface roughness and void, as illustrated in Fig.2(b). Since EMA model is better at handling this type of non-uniform surfaces, it is chosen to characterize the Pd thin film. The film thickness and void content fitted at 200-800nm wavelengths are shown in Fig.4. From the graph, it is estimated that the GPC of Pd film is about 1.30±0.02Å/cycle.

In general, the void percentage reduces with the increase of cycle numbers. In our experiment, the void percentage reduces to about 40% for over 100 cycles. This is in agreement with the experiment SEM image (inset), where 3D island-like particle is retained on the silicon substrate even after 200 cycles. However, it should be stressed that the void content at large cycle numbers should be only taken qualitatively, as with increased Pd concentration on the surface, severe light absorption happens on the surface, leading to attenuation of the reflected light and larger errors in the measurements. More experiments and refined models taking into account the correction due to light absorption are needed in future work. Overall, compared with the standard Pd model (which takes the film's refractive index as an constant) and Cauchy model (which takes the film as a smooth layer), EMA model still provides better and more robust results, especially for Pd films grown with small number of ALD cycles, where attenuation of reflected light is negligible.

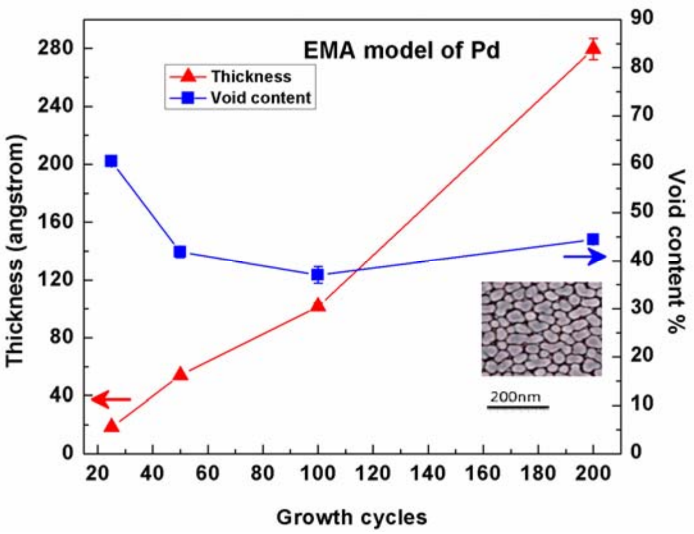

Fig.4 Void content of different thickness Pd

CONCLUSIONS

Here we report the SE characterization of Al_2O_3 and Pd thin film grown by ALD. For Al_2O_3 thin film, we have compared the results of Cauchy and EMA model. In Cauchy model, the wavelength range of the fitting matters and some empirical ranges are revealed in this article. In comparison, EMA is effective and feasible in characterizing ultrathin film as it takes void content and surface roughness into consideration. For Palladium thin films, our preliminary work shows that EMA model fits with the experiment data.

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