High Accuracy Determination of the Density of Pt Thin Films by Comparative Measurements of X-ray Reflectivity and Gravimetry

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(Received January 12 1998; accepted January 18 1998)

Comparative results are presented for the density of Pt thin films by using grazing incidence x-ray reflectivity (GIXR) and gravimetry techniques. GIXR results showed that the errors in the 9.96 nm Pt film are only 1.9%, 0.5% and 2.2% for the density, thickness and surface roughness, respectively. For the Pt thin films with thickness between 5 and 100 nm, GIXR measurements are in good agreement with those obtained from gravimetry. Their difference is within 1.5%. With the high resolution of GIXR, a slight density decrease in the ultrathin film(5 nm) was successfully detected. The factors that affect the accuracy and the reliability of density measurement in GIXR are also discussed.

1. INTRODUCTION

Polycrystalline metallic thin films have attracted much interest due to their extensive applications in electronic, magnetic, and optical devices [1-4]. Particularly, the highly reliable electrodes of metallic thin films are required in semiconductor devices with the ultralarge-scale integration [5]. The performance of metallic thin films is strongly affected by their internal and surface structures. Therefore, a highly accurate determination of their structural parameters, such as density, thickness, surface and interface roughness, is becoming increasingly important.

Grazing incidence x-ray reflectivity (GIXR) has been recognized as a rather promising technique for the characterization of thin films in the last few years, because of its non-destructive and quantitative nature[7-10]. In their pioneering work, Wainfan et al. [11] have tried to measure the density of thin copper films, by combining X-ray reflection measurement and chmeical determination of the mass of copper films. Because of the limitation of their aligning precision, the errors of the density measurement were about 10%. In a recent paper, Schalchli et al. [12] presented the accuracy, as high as ±0.7%, of density measurement with GIXR technique while they studied the dependence of density as a function of the thickness of silica thin films made by ultraviolet-induced chemical vapor deposition. Although the measurement accuracy has been listed and discussed in previous studies [11-13], no result has been compared with other direct and reliable methods. Hence, the real accuracy and reliability of GIXR are still unknown.

Gravimetry is one of the most reliable methods to determine the density of uniform thin films, providing the thickness and the area of films are known. In this work, we aim to determine the accuracy and reliability of GIXR by comparing with the gravimetric measurement results. It should be mentioned that the system of Pt thin film on SiO_2 substrate is very suitable for gravimetry with high accuracy, since metal Pt has a higher density and is stable in air. We present the density data of Pt thin films measured by GIXR, which is found in good agreement with those obtained by gravimetry. We conclude that GIXR has a very high accuracy to determine density of thin films.

2. EXPERIMENTAL

The Pt thin films with the thickness of 5, 10, 30 and 105 nm, were grown on a 76.2 mm-diameter and 0.5 mm-thick ultrasmooth SiO_2 wafer by means of molecular beam epitaxy (MBE) at room temperature, respectively. The MBE system employed in this study

was designed to achieve uniform thin films over a 76.2 mm diameter wafer with less than 0.8 % deviation in thickness by properly adjusting the relative distance and position between the substrate and the e-beam guns, and rotating the substrate during deposition at about 10 rpm. The growth temperature can be controlled between room temperature and 1000°C. A detailed system performance will be described elsewhere [14]. The growth rate was about 0.10 nm per second.

The SiO_2 wafers were weighed before and after thin film deposition using a precisely calibrated micro-balance with a sensitivity of 1 μg (MT-5, Mettler). The weight of the samples was corrected by considering the floating force in air. A flat-bed type scanner operating in transmission mode was used to estimate the area of the Pt films. The Pt deposition area was calibrated with a scanned image of a scale. Since the substrate is the SiO_2 wafer, the contrast between the Pt film and the substrate is sufficiently high to determine the film area.

GIXR measurements were performed by a high resolution 18 kW rotating anode x-ray diffractometer (Rigaku SLX-2000). The working voltage was 40kV and current was 200mA. The X-ray beam from the rotating anode Cu target is monochromatized by a Ge(220) channel-cut monochromator. The X-ray reflection intensities were collected by a scintillation counter. To increase the resolution, an incident collimating slit of 50 μm in width and a receiving slit of 50 μm in width were used. The sample was mounted on a vertical sample stage as schematically illustrated in Figure 1. For the precise alignment of the sample position, the sample stage is fixed on a high resolution goniometer, which has the precision of 0.0001° for rotating sample position ω and 0.0002° for detector position 2θ. The scanning rate was 0.010°/min, and the step size was 0.002°.

3. RESULTS

A rocking scan in total reflection area was shown in Figure 2. During the measurement, the detector position (2θ angle) was fixed at 0.7000° and the scanning step was 0.0001°. It can be seen that a very sharp and symmetric total reflection peak appears in the range of 0.6374~0.6491°. The peak position is at 0.6432° and its half width is 0.0059°. A very small ω angle deviation within ±0.0003° can be obtained by repeating alignments. It suggests that there is a very high accuracy in determining ω angle in the GIXR measurements of this work.

The x-ray reflectivity spectra of Pt thin films with thickness of about 5, 10, 30, 105 nm were shown in

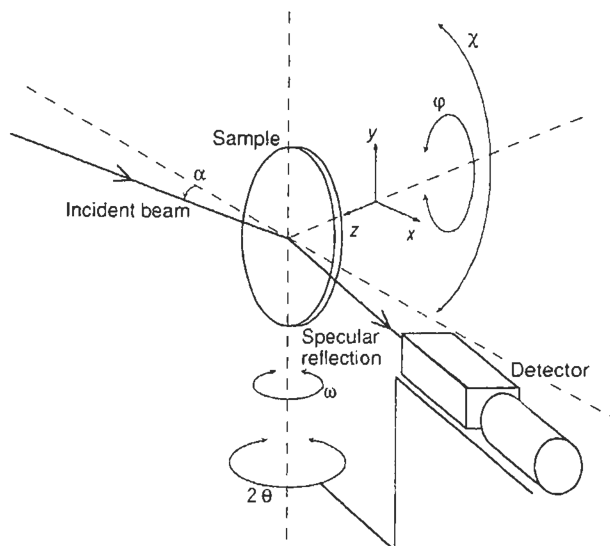

Fig.1 A schematic drawing of grazing incidence x-ray reflectivity measurement.

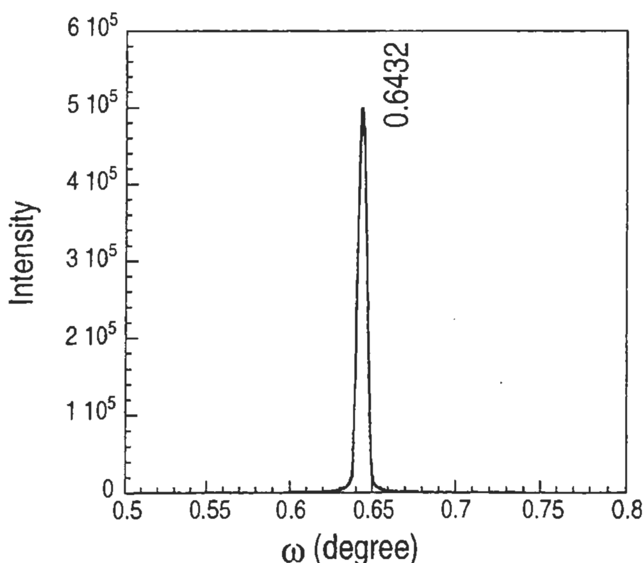

Fig. 2 A rocking scan in total reflection area, by placing the detector at a fixed angle (0.7° and rotating the sample.

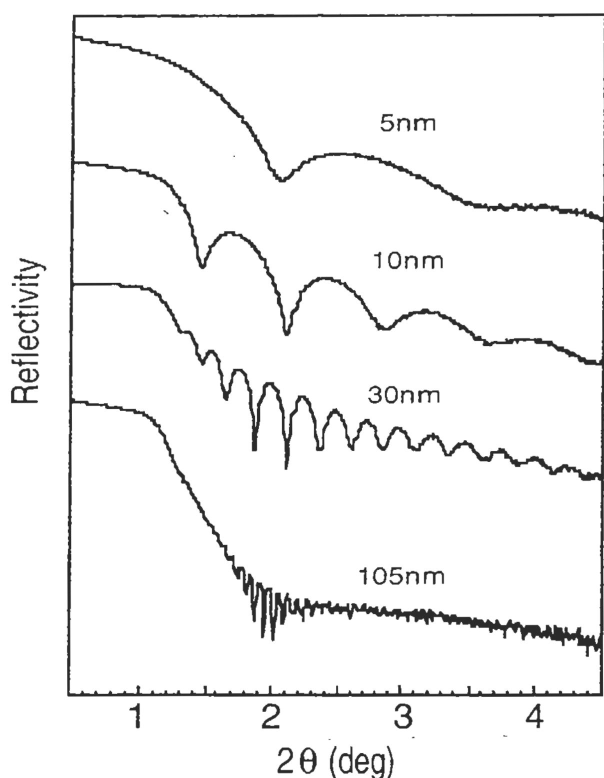

Fig. 3 Reflectivity spectra for the Pt thin films with thickness of 5, 10, 30 and 105 nm.

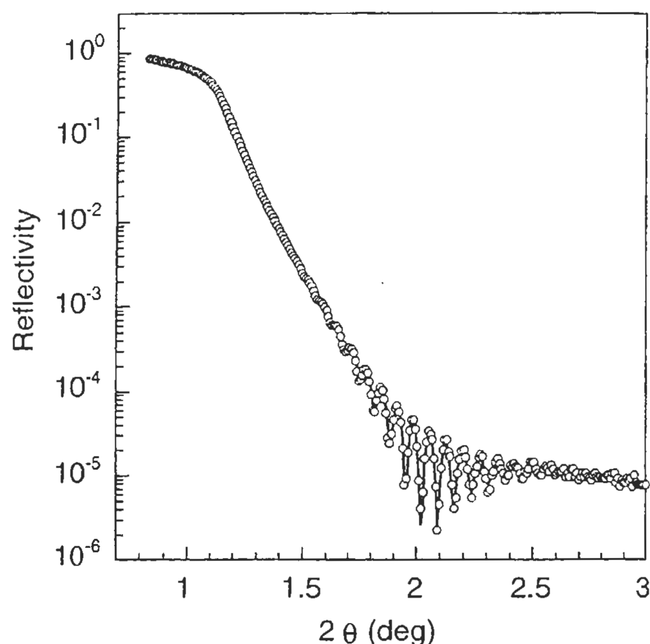

Fig. 4 Reflectivity spectrum for the 105.27 nm Pt thin film: the circles represent the experimental data, and the solid line represents the fitting curve.

Figure 3. It can be found that there are significant differences in their GIXR spectra. The oscillation frequency becomes smaller as the thickness becomes thinner. In the 2θ range of 0.5~5.0°, only two oscillation peaks appear for 5 nm-thick Pt ultrathin film. However, 10 stronger oscillation peaks can be observed in the region between 1.6° and 2.4° for the Pt thin film with thickness of 105 nm. The oscillation intensity gets lower and reaches to the same level as the noise in the higher angle region.

Figure 4 demonstrates the normalized GIXR spectra of both the experimental and the fitting data for the film of 105 nm in thickness. It can be seen that the fitting curve is quite identical with that of the experimental one. The total intensity decays by 5 orders of magnitude from 1.0° to 3.0°, indicating that the sample has a rougher surface.

Table 1 summarizes the fitting results for the Pt thin films obtained by GIXR and gravimetry. The error was defined as the double of a standard deviation. Every sample was measured for five times. The results clearly show that both GIXR and gravimetry give the identical density for the same sample within the error, 1.8%. The density of 105.27 nm Pt thin film is 20.30 $g{\cdot}cm^{-3}$, which is about 94% of the density of bulk Pt(21.45$g{\cdot}cm^{-3}$). The density of 73.98 nm Pt thin film grown at 1073 K is 21.31 g·cm-3, which is closer to the bulk one.

4. DISCUSSIONS

The density ρ of thin film materials obtained from GIXR can be expressed as:

$$\rho = (2\pi m c^2 M)\,\delta / (e^2 \lambda^2 N_0)(Z + f') \qquad (1)$$

where m is the static mass of an electron, c is the speed of light in vacuum, M is the atomic weight, e is the elementary charge, λ is the x-ray wavelength, N_0 is the Avogadro constant, Z is atomic order of element, f′ is the real section of scattering factor [15], and δ is the real section of refractive index. The refractive index can be commonly expressed as $n=1 - \delta - i\beta$. δ is proportional to the square of the critical momentum-transfer vector k_c^2,

$$k_c = (4\pi/\lambda)\sin(\theta_c) \qquad (2)$$

where θ_c is the critical angle. Seen from equation (1) and (2), the density accuracy of GIXR measurement is mainly affected by the determination of θ_c value.

Table I The structural parameters of thin Pt films as measured by GIXR and gravimetry

		X-ray reflectivity				Gravimetry	
	T(K)	density(g/cm^3)	density percent to bulk Pt	thickness (nm)	roughness (nm)	density(g/cm^3)	density percent to bulk Pt
sample 1	300	18.85±0.35	87.8%	5.02±0.02	0.90±0.01	18.60±0.60	86.7%
sample 2	300	20.28±0.39	94.5%	9.96±0.05	0.91±0.01	20.15±0.30	93.9%
sample 3	300	20.20±0.35	94.2%	30.11±0.20	1.15±0.03	19.90±0.16	92.8%
sample 4	300	20.30±0.37	94.6%	105.27±0.29	2.11±0.05	20.01±0.16	93.3%
sample 7	1073	21.31±0.30	99.3%	73.98±0.22	1.68±0.03	21.14±0.20	98.6%

The errors are defined as the double of standard deviation.
T represents the growth temperature of Pt films.

The θ_c value was optimized by the Als-Nielsen's x-ray specular reflection expression during the least-square fitting [16]. Therefore, it means that the instrument alignment is the most important limiting factor in precisely determining the density of thin film by GIXR method. A misalignment of 0.005° in sample tilt α with respect to the incoming x-ray beam, can change the final value of the electron density by 5% [17]. The reason is that the critical momentum-transfer vector k_c is incorrectly determined by the critical angle $\theta_c + \alpha$. In our GIXR measurement as shown in Fig. 2, a very high alignment precision as good as ±0.0003° has been routinely achieved. This leads to very small experimental deviations. In fact, our results show that the GIXR experimental errors were about 0.37g/cm^3 in density (corresponding to 1.8%), 0.29nm in thickness (0.27%) and 0.05 nm in surface roughness (2.3%) for the 105.27 nm Pt films in Table 1.

Cowley et al. noted that the substrate departuring macroscopically from flatness could seriously degrade the resolution of a conventional reflectivity measurement[18]. They reported that part of the surface was misaligned by up to 0.1° on a rippled and beveled Si surface. The integrated intensity of reflectivity became wide and asymmetric. However, a sharp and symmetric reflection in Figure 2 shows that the surface of Pt thin film on SiO_2 ultrasmooth substrate is very flat. It ensures that the misaligning error is very small during the adjustment.

Figure 5 compares the densities of Pt thin films obtained by the two methods. It indicates that the densities determined by GIXR are very close to those of gravimetric measurements. Although the GIXR density is always a little larger than that of gravimetric method for the same Pt thin film, the maximum density difference was about 1.5% between the GIXR and gravimetry results. This deviation is smaller than the maximum GIXR measurement error (1.9%). The results confirm that both GIXR and gravimetric methods have the identical density for the Pt thin films. The measurement accuracy of gravimetry is affected by the determination of weight, area and thickness. For the 105.27 nm Pt film, the weight and area are about 2000 μg and 1000 mm^2 respectively, The weight error is about 0.2% and area error is 0.3%, considering the measurement precision from micro-balance and scanner. The GIXR thickness error of 105.27 nm Pt film is 0.3% in table 1. The total errors are about 0.8% for 105.27 nm Pt film by gravimetric method. In a previous paper [9], we evaluated the thickness of a SiO_2/Ta_2O_5 multilayer film with a total thickness of 100 nm using both GIXR and transmission electron microscopy. The total thickness difference between the two methods was lower than 2.6%. It is fully possible to obtain a smaller error for a single layer Pt film with GIXR method.

For the Pt films grown at room temperature, the densities almost maintain constant around 20.30 g/cm^3

within the experimental error ± 0.39g/cm^3, with thickness varying from 105.27 to 9.96 nm. The density is about 94% as that of bulk Pt. However, the density abruptly decrease to 18.85 g/cm^3 for 5.02 nm Pt ultathin film, which is only 87.8% as that of bulk one. Wainfan [11] and Tsuji [19] have reported that the densities of Cu and Au films decreased as their thickness became thinner. The densities of 5nm-thick Cu film and 40 nm-thick Au film are only 80% and 73% of their bulk one, respectively. Tsuji et al. [19] simply explained that the lower density was attributed to the evaporated Au film being very porous. Liu et al. [20] studied the microstructure of the Cr underlayer using the transmission electron microscopy. They found a large proportion of gaps with a width of 1-3 nm between the Cr grain boundaries in initial growth process. It is possible that there are some gaps between the grain boundaries in very thin Pt film, since the Pt film is island growth at room temperature [21, 22].

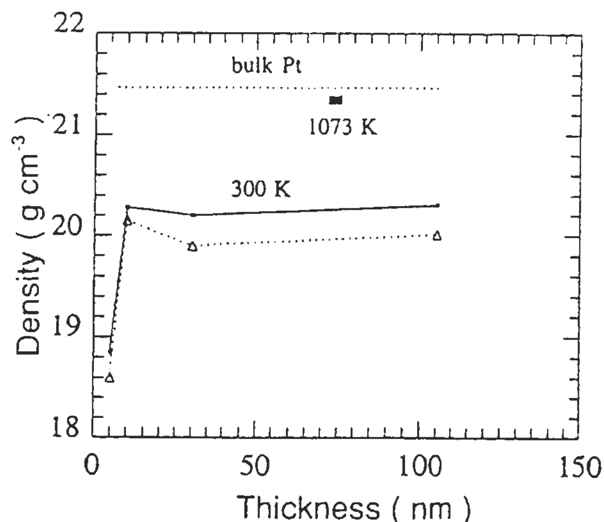

Fig. 5 A comparison of the density obtained from GIXR (open square) and gravimetry(line with triangle) methods.

5. CONCLUSION

We have shown the measurement results of density of Pt thin films with both GIXR and gravimetry methods. Within errors of measurement, two methods are in good agreement. It confirmed that high resolution GIXR measurement can provide a highly accurate way to determine density of thin films. In addition, GIXR method can also provide very accurate data for thickness and surface roughness of thin films.

ACKNOWLEDGMENT

We Would like to thank Dr. E. Horn for his helpful discussions and suggestion. One of the authors (B.L.) is grateful to an AIST fellowship for the financial support during his stay in Japan.

REFERENCES

1. S.Yu. Shiryaev , F. Jensen, J. Lundsgaard Hansen, J., Wulff Petersen , and A. Nylandsted Larsen, Phys. Rev. Lett., 78(1997) 503.
2. D.E. Jesson, K.M. Chen, S.J. Pennycook, T. Thundat, and R.J. Warmack, Science, 268 (1995) 1161.
3. L.M. Terman, Appl. Surf. Sci., 117-118 (1997) 1.
4. A.K. Kulkarni, L.C. Chang, Thin Solid Films 301 (1997) 17.
5. K. Temst, M.J. Bael, B. Wuylts, C. Van Haesendonck, Y. Bruynseraede, D.G. de Groot, N.Koeman, and R. Griessen, Appl. Phys. Lett. 67 (1995) 3429.
6. M. Chladek, V. Valvoda, C. Holy, and J. Grim, Appl. Phys.Lett. 69 (1996) 1318.
7. E. Chason and T.M. Mayer, Critical Reviews in Solid State and Materiala Science, 22 (1997) 1.
8. B.K. Kellerman, E. Chason, D.P. Adams, T.M. Mayer, and J.M.White, Surface Science, 375 (1997) 331.
9. I. Kojima, B.Q. Li, T. Fujimoto, K.J. Kim, and D.W. Moon, J. Phys. D: 30 (1997) 2143.
10. N. Awaji, S. Ohkubo, T. Nakanishi, Y. Sugita, K. Takasaki, and S. Komiya, Jpn. J. Appl.Phys., 34, 1013 (1995); 35 (1996) 67.
11. N. Wainfan, J. Scott Nancy, and L.G. Parratt, J.Appl.Phys., 30 (1959) 1604.
12. A. Schalchli, J.J. Benattar, and C. Licoppe, Europhys. Lett. 26 (1994) 271.
13. M.F. Toney and S. Brennan, J. Appl. Phys. 66 (1989) 1861.

14. to be published.
15. D.T. Cromer and D. Liberman, J. Chem. Phys., 53(1970)1891.
16. J. Als-Nielsen, Structure and dynamics of Surfaces, edited by W. Schommers and P. Blankenhagen, (Springer-Verlag, Berlin, 1986), p.181.
17. W.E. Wallace and W.L. Wu, Appl.Phys.Lett. 67 (1995) 1203.
18. R.A. Cowley and T.W. Ryan, J. Phys. D: 20 (1987) 61.
19. K. Tsuji and K. Hirokawa, Spectrochimica Acta 48B (1993) 1471.
20. Y. Liu, B.W. Robertson, Z.S. Shan, S.H. Liou, and D.J. Sellmyer, J.Appl.Phys. 77 (1995) 3831.
21. H. You, K.G. Wuang, and R.T. Kampwirth, Physica B 221 (1996) 77.
22. H. You, R.P. Chiarello, H.K. Kim, and K.G. Vandervoort, Phys. Rev. Lett. 70 (1993) 2900.

質疑応答　　査読者：二澤（理学電気）
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二澤：高い精度で密度が評価されていて、興味深い内容でした。
少々質問があります。

(1) substrate に ultrasmooth SiO_2 を使用されていますが、これ自身の表面粗さ (roughness) は評価されていないのでしょうか。

著者：ＡＦＭを用いて測定しております。測定結果はrmsで0.3nm程度でした。Ｘ線反射率測定でも同程度の結果が得られますが、ＡＦＭとＸ線反射率による粗さ評価については別の機会に発表したいと考えています。

(2) rocking scanはすべての試料で行ったのでしょうか。

また、5nmの試料ではisland状に成長して、gapがあるため密度が小さいと結論づけています。この試料でもピーク形状に大きな変化が見られなかったのでしょうか。islandがあるとピークの巾が広がるような気がするのですが。変化が無かったとすればislandの面の傾きがそろっていると考えることが出来るのでしょうか。

著者：すべての試料について行っております。Ｘ線反射率測定の前に、試料の位置を最適化します。そのプロセスに rocking (ω) scan が含まれており、その形状を確認した後測定を始めています。しかし、通常、データは保存しておりません。Ｘ線反射率測定の信頼性は、試料のマクロな平坦さに強く依存します。ω scanがそのチェックになるために行っているわけです。

ご質問にある islandのサイズがω scanのピーク形状に影響を与えるかどうかは定かではありません。ただし、もし影響があっても極わずかです。また、Ｘ線回折の測定では、薄膜は [111] 方向に選択成長していることがわかっています。

古川：Ｘ線の全反射領域を利用する様々な解析、例えば薄膜表面の構造解析に用いるＸ線回折法、表面層や表面汚染分析のための全反射蛍光Ｘ線分析法、結晶表面・界面での原子の位置や表面での吸着の状況などを知ることのできるＸ線定在波法などの手法は、表面・界面の原子、分子レベルの制御および評価、あるいはまた数原子層の超周期構造と電子素子特性との関係の研究に対し有用な計測法の１つである。今後、更に利用が盛んになる解析方法と思われる。この意味でＸ線の全反射領域を利用する薄膜材料の密度測定に関する本論文は、精密測定に対する条件や測定精度の検討に取り組んだ点で意義が大きい。特に薄膜材料の微構造に関し間接的に構造情報を与えるので、Ｘ線回折法では情報を得にくい結晶性の低い薄膜材料の解析や材料の一部しか観察できない透過型電顕による薄膜材料の解析に有用な知見を与える方法であると思われる。

著者：Ｘ線反射率測定は全反射領域よりはむしろ内部に進入し始める角度での情報を利用する方法です。特に薄膜の厚さに関しては、透過電顕の２～３％程度の精度に対して、１％より良い精度（再現性）を与えます。

古川：確認したい事項
(1)　幾つかの物理定数や測定値から計算した結

果をTable 1に示されていると思われますが、数値の桁数が3桁のものから5桁のものまで存在しています。有効桁数に言及し、可能なら統一されると良いと思われます。

(2) 測定誤差の検討に標準偏差値を取り扱うなど統計的な処理を行っておられますが、全反射法あるいは重量法ではそれぞれ測定の回数は幾つなのでしょうか、つまり測定のn数は幾つなのでしょうか、差し支えなければ記載された方がよいと思われます。

(3) 膜厚の5，10，30，105nmは実測値ではなくdeposition速度から割り出した数値と思われます。膜厚測定のために表面を別の材料で保護(蒸着やスパッタコーティング)した上で劈開により断面を露出させ、走査電顕などで実測できると確度が向上すると思われますがいかがでしょうか。

(4) 最高の全反射強度を与える反射角(臨界角)は0.6432／2度と思われます。本臨界角と用いた酸化珪素基板（SiO_2）に対する計算値よから求めた臨界角はほぼ一致するのでしょうか。あるいはPt薄膜が存在して場合、酸化珪素基板（SiO_2）との臨界角は意味がないのでしょうか。つまり最高の全反射強度を与える本反射角の場合、X線の進入深さはどの程度になるのか、そして情報深さであるX線の表面からの侵入深さはそれぞれのPt膜厚5，10，30，105nmの全深さ領域を含んでいるのか確認したいところです。

(5) 測定された密度と成膜された膜厚との関係に言及され微構造の影響が大きいと推論されておられます。確かに組織との関係も十分考慮しなければならないと思われますが、Pt膜の平面における4方向に存在する端面は基板表面から垂直に立ち上がりそして表面では90度の角度で最表面つながっているのでしょうか。つまり直角状の幾何学的に成長しているのでしょうか。そうではなく傾斜の付いた土手の形状を呈する、あるいは台形状になっている可能性はないでしょうか。仮に直線的にせよ不定形状にせよ傾斜が付いておれば、面積とそれから計算された体積とに差が生じ、面積の取り方にもよりますが、実際より高め或いは低めの値となる思われますがいかがでしょうか。端面をAES装置で電子線走査し強度変化を測定するか走査型電顕で確認することは大変興味深いと思われました。

また、最も膜厚の小さい5nmの場合、密度が他と比較して低いのですが、たとえPtといえども極薄い酸化膜が存在しており、その表面酸化膜の影響が顕著に現れているという可能性は無いのでしょうか。XPSなどでの確認はされましたでしょうか。

著者：以下、部分的にまとめてご回答します。

(1)、(2)：測定回数はX線反射率、質量測定について5回です。面積は2回測定しています。質量および面積の誤差は、本文中にもありますが、薄膜の物理的パラメーターに影響を与えません。また、論文中に記載されていますが、Table 1中のパラメータに付加された誤差は、標準偏差の2倍です。ただし、Table 1では、互いの数字を比較しやくすするために小数点2桁まで表示しています。この意味は、例えば厚さを見ていただけると、誤差は0．5%より小さいことがわかります。また、密度について比較すると、X線反射率では同様な数字を示しますが、重量法では当然ですが重さに従って大きく変わります。

(3)：X線反射率曲線の解析による実験値です。電子顕微鏡よりは高い再現性で評価できます。

(4)：X線反射率ではX線の試料表面に対する軸だしがきわめて重要です。これが全てであるといっても過言ではありません。従って、測定前に常に全反射領域の角度において試料の最良の配置を決める必要があります。rocking scanの形状は次に始めるX線反射率測定の信頼度の指標になるわけです。この意味で図示しました。また、X線の侵入深さは角度に依存しますが、X線反射率曲線には十分に深い領域まで含まれています。

(5)：今回の試料では、蒸着膜の周囲の形状は薄膜のパラメータ評価にほとんど影響しません。十分に急峻であるということです。また、表面汚染については、絶対的な評価はできていませんが、大きな影響はありません。XPSはもちろん測定しています。むしろ、水分の吸着量や小さなパーティクルが問題かも知れませんが、X線反射率と重量法に見られる系統誤差と併せて現在検討中です。