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Surface roughness and island formation effects in ARXPS quantification

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Quantification of surface nano-structures by angle-resolved XPS (ARXPS) is straightforward and works quite reliably for perfectly flat surfaces of amorphous materials. For rough surfaces, the interpretation of ARXPS is, however, complicated because the angular variation of the XPS peak intensity depends on the surface roughness. Even for ideally flat substrates, ARXPS analysis of laterally inhomogeneous surface structures grown on the surface is quite complex. The reason is that neighboring nano-clusters shadow the XPS peak intensity. The effect depends on cluster shape as well as the distribution of clusters on the surface. In addition the effects depend on the flatness of the underlying substrate. The interpretation of ARXPS then becomes quite complex. In the present paper, we have studied this problem by analyzing ZnO nano-clusters grown on substrates of SiO_2 and Al_2O_3. Thus we compared the results of quantification by the four techniques: ARXPS, XPS-peak shape analysis, Rutherford backscattering spectroscopy and x-ray fluorescence spectrometry. While the latter three techniques gave consistent results, the results of the ARXPS analysis were way off. This deviation is discussed in terms of the above-mentioned shadowing effect of neighboring clusters as well as roughness of the underlying substrates. Different normalization methods in the ARXPS analysis procedure are compared and it is found that some of the observed problems for the substrate peaks (but not for the peaks from the overlayer film) can be reduced by applying reference samples with similar roughness for normalization of the data. In conclusion, the ARXPS technique is very much dependent on surface roughness as well as on the morphology of the thin films. Thus for reliable quantification with ARXPS it is necessary to have independent knowledge on surface roughness as well as the distribution of islands of the thin films. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ARXPS; quantitative XPS; surface roughness; ZnO; island growth

INTRODUCTION

Reliable quantification of surface nano-structures is extremely important for present day technological developments. In a recent study,[1] we compared the three techniques: XPS-peak shape analysis, Rutherford backscattering spectroscopy (RBS) and x-ray fluorescence spectrometry (XRF) for their ability to consistently determine the total amount of Zn atoms in ~1 nm–10 nm thin ZnO films grown on the three substrates: SiO_2, Al_2O_3 and an Al foil with a thin Al_2O_3 layer. The relative values were found to be consistent to within ~15–20%. In this paper we compare these results to an analysis of the same samples with angle-resolved XPS (ARXPS).

ARXPS has been available for many years as a technique for non-destructive analysis of surface structures[2–7] and progress has also been made in the incorporation of elastic scattering effects.[8,9] The problems encountered for rough surfaces has also been the topic of several papers.[10,11] Quantification of surface nano-structures by ARXPS is straightforward for perfectly flat surfaces of amorphous solids where diffraction and forward focusing effects can be neglected.

For rough surfaces, the interpretation of ARXPS is complicated because the angular variation of the XPS peak intensity depends on the surface roughness. Even for ideally flat substrates, ARXPS analysis of laterally inhomogeneous surface structures grown on the surface is quite complex. The reason is that neighboring nano-clusters cause shadow for the XPS peak intensity. The effect depends on cluster shape as well as on the distribution of clusters on the surface. In addition, the effects depend on the flatness of the underlying substrate. The interpretation of ARXPS may then become quite complex. The problem was addressed recently in detail.[11]

In this paper, we have studied this problem by analyzing ZnO nano-clusters grown on substrates of SiO_2 and Al_2O_3. These substrates have different surface roughness. Thus we have compared the results of quantification by the four

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techniques: ARXPS, XPS-peak shape analysis,[13,14] RBS and XRF. The first two techniques can give information on the in-depth distribution of atoms. However, all four techniques can determine the amount of atoms within the surface region of the samples and we have therefore compared the results for this quantity determined by the four techniques. We denote this by AOS_{ARXPS}, AOS_{QUASES}, AOS_{RBS}, and AOS_{XRF}, respectively.

EXPERIMENTAL

Sample preparation

Nanometric ZnO films of thickness ~1 nm–10 nm were deposited by decomposition of a volatile Zn organometallic precursor ($Zn(C_2H_5)_2$) in a microwave plasma of oxygen at room temperature.[15] Two different substrates were used: SiO_2 thermally grown (~100 nm thick) on Si(100), and a single crystal of sapphire (α-Al_2O_3). They were cleaned by 3 keV O_2^+ bombardment until complete removal of surface carbon contamination as determined by XPS. The size of the substrates was ~1 cm × 1 cm.

Deposition of ZnO was performed simultaneously on both substrates to produce four sets of samples, one after each deposition process. Thus, each set of samples contains approximately (but not necessarily exactly) the same amount of deposited ZnO. Details of the sample preparation as well as the XPS peak shape analysis (using the QUASES-Tougaard software[12]), RBS and XRF analysis are given in Reference 1.

Angle-resolved XPS measurements

After film growth, the samples were transferred without exposure to air to the XPS analysis chamber (base pressure $\sim 5 \times 10^{-10}$ mbar). Here, x-ray excited photoelectron and Auger electron spectra were recorded with a VG-Escalab 210 electron spectrometer. The surface was irradiated with Mg K_α x-rays. The emitted electrons were collected with 50 eV pass energy. The surface area analyzed was a circle of ~1 mm diameter. Energy scans of Zn $2p_{3/2}$ and Zn 3p peaks from the ZnO deposits and for Si 2s and Si $KL_{2,3}L_{2,3}$ and Al 2s and Al $KL_{2,3}L_{2,3}$ peaks from the substrates were recorded for the following angles with respect to the surface normal: $\theta = 0$, 30, 45, 55 and 65° obtained by tilting the sample. The angle between detector and x-ray beam was fixed at 54°. The angle in the horizontal plane (normal to the electron detection) between the projection of the x-ray source and the axis of sample rotation was 45°.

The peak intensity was determined subtracting a straight line over the extent of the main peak structure. From the empirical TPP-2M formula[16] for electrons traveling in ZnO, we have determined and used the following values for the inelastic electron mean free path λ: 0.74, and 2.3 nm for the Zn $2p_{3/2}$ and Zn 3p peaks from the ZnO deposits; 0.65, and 2.3 nm for the Zn $2p_{3/2}$ and Zn 3p peaks from the Zn; 2.2, and 2.9 nm for the Si 2s and Si $KL_{2,3}L_{2,3}$ peaks from the SiO_2 substrates; and 2.2, and 2.6 nm for the Al 2s and Al $KL_{2,3}L_{2,3}$ peaks from the alumina substrates, respectively.

RESULTS AND DATA ANALYSIS

We have used the QUASES-ARXPS software package[12] for data analysis. This software gives the possibility of using three different ways of normalizing the data and automatic determination of that structure which gives the minimum least squares deviation from the experiment. The software also has an option to include elastic electron scattering effects. First we discuss general aspects of the ARXPS method.

It is well known that for flat surfaces, in the straight line approximation and assuming that the analyzed area varies as $1/\cos\theta$ the measured photoelectron intensity $I(\theta)$ is given by

$$I(\theta) = \frac{A_0(XF, DF)}{\cos\theta} \int_0^\infty dz\, f(z) \exp\left(-\frac{z}{\lambda\cos\theta}\right) \quad (1)$$

where $f(z)$ is the concentration profile that includes the in-depth distribution and atomic concentration of a given element, and A_0 is a function that includes the dependencies on the detector efficiency (DF) and the excitation probability (XF) (photon flux density, photoelectron excitation cross-section).

Thus, the intensity recorded for a flat solid with homogeneous depth distribution (i.e. $f(z) = 1$) is $I_{\text{flat homogeneous sample}} = A_0(XF, DF)\lambda$

The dependency on the photon flux and cross-sections cancels out if we normalize the intensities $I(\theta)$ to intensities of the same peak taken at the same angle but from a reference sample $I_{\text{ref}}(\theta)$ with a homogeneous in-depth distribution. Specifically the experimentally determined ratio is compared to the following expression

$$\frac{I(\theta)}{I_{\text{ref}}(\theta)} = \frac{\int_0^\infty dz\, f(z) \exp\left(-\frac{z}{\lambda\cos\theta}\right)}{\lambda\cos\theta} \quad (2)$$

The in-depth profile (given by the island coverage c and height h) is determined by a least squares optimization procedure and AOS_{ARXPS} is then the product of c and h.

Analysis of pure, homogeneous samples

We start with analysis of the spectra from pure Zn, ZnO, Al_2O_3 and SiO_2 samples for which we know that the depth distribution is homogenous. The measured XPS intensity will depend on geometrical factors because the intensity per unit area of the exciting x-ray beam as well as the analyzed surface area will change as the sample is tilted. Since these effects are the same for all peaks from a given sample they are removed by taking the ratio of two peaks from the same solid.

Figure 1 shows the relative peak areas determined in this way. The above-mentioned geometry effects are cancelled by this normalization and the intensity ratio should be constant independent of the angle of emission. Figure 1 shows that they vary by ~5% to ~20% for the largest emission angles. Note that it is well known that ARXPS analysis is strongly affected by uncertainties of only a few % in the peak intensities[7] so this discrepancy of the expected values for the homogeneous sample will lead to a large error in the quantification.

The observed variation with angle of emission could be due to surface roughness, elastic electron scattering,

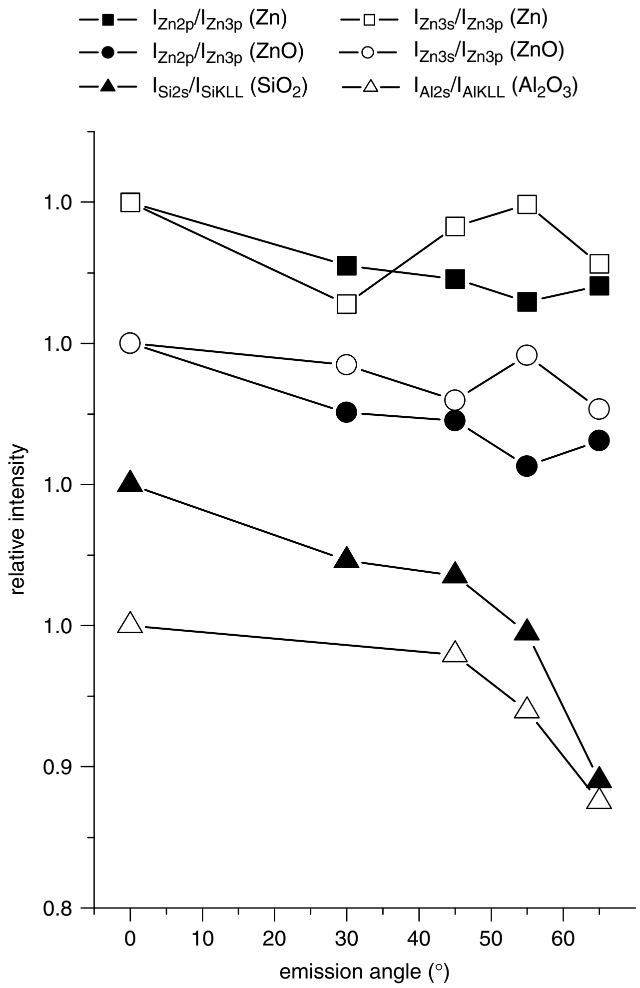

Figure 1. Ratio of peak areas from pure Zn, ZnO, Al_2O_3 and SiO_2 samples for which we know that the depth distribution is homogenous. The geometrical factors due to the intensity per unit area of the exciting x-ray beam as well as the analyzed surface area changes as the sample is tilted. Since these effects are the same for all peaks from a given sample they are removed by taking the ratio of two peaks from the same solid and ratios should be constant independent of the emission angle. The reason for the observed variations is interpreted as being due to surface roughness.

and/or surface excitations. We may expect to enhance surface excitations when considering larger angles of emission[17] but it is difficult to estimate qualitatively the size of this effect.

The magnitude of the effect of elastic electron scattering can easily be quantified with the QUASES-ARXPS software package which uses the algorithm of Nefedov.[9] The effect is largest for the largest angles of emission. But even at 65° for the pure, semi-infinite substrates the effect was negligible for SiO_2 and Al_2O_3 and less than 5% for Zn and ZnO. So elastic scattering can be excluded as a main contribution to the effects observed in Fig. 1.

Another possible source might be surface roughness and film morphology. To understand this effect we propose a simple model as shown in Fig. 2. Let us consider peaks at two energies E_1 and E_2 which for a flat surface would give the intensities I_1 and I_2. For a given angle of emission, the electrons will have traveled the extra distance Δ due to surface roughness. The ratio of the two peak intensities is then

$$\frac{I_1^{\text{rough}}}{I_2^{\text{rough}}} = \frac{I_1 e^{-\Delta/\lambda_1}}{I_2 e^{-\Delta/\lambda_2}} = \frac{I_1}{I_2} e^{-\Delta \frac{\lambda_2 - \lambda_1}{\lambda_1 \lambda_2}} \tag{3}$$

Now the two peaks are from the same material but at energies $E_1 < E_2$ and therefore $\lambda_1 < \lambda_2$. The correction to the intensity ratio in Eqn (3) is therefore smaller than 1 in accordance with the results in Fig. 1. As an example, suppose $\lambda_1 = 1.3$ nm and $\lambda_2 = 1.0$ nm. Then with $\Delta = 1$ nm the ratio is ~0.8, in good agreement with the results in Fig. 1. This simple model shows that the observed variation in Fig. 1 can easily be explained by surface roughness.

Note that up to this point we have not considered the unknown samples, but just studied different sources of uncertainties in the analysis of the data from the homogeneous reference samples where one would have expected the quantification to be straightforward.

Analysis of the thin ZnO films

The comparison (from Reference 1) between the results for the amount of substance of Zn in the two sets of samples by XRF and RBS are plotted in Fig. 3 against the AOS determined by QUASES-XPS-peak shape analysis. Note that the consistency of the relative thicknesses is very good. The previous analysis made by XPS peak shape analysis[1] showed that the ZnO grows in the form of islands. This will give rise to a shadowing effect which depends on the details of the shape and distribution of the aggregates.[10,11]

In order to improve the resulting analysis by ARXPS we then tried to minimize the roughness effect in the quantification by normalization of data taken from the same

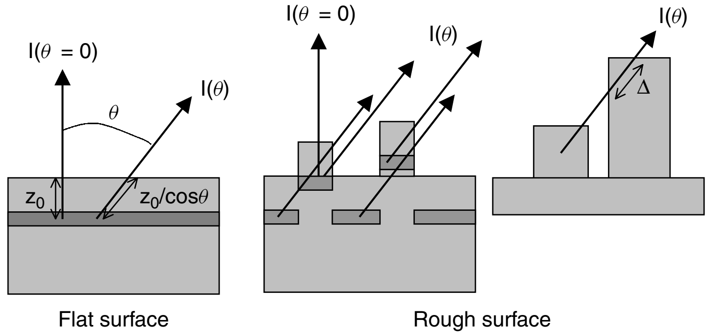

Figure 2. Simple model of the effect of surface morphology. This model explains qualitatively the observed variation in Fig. 1.

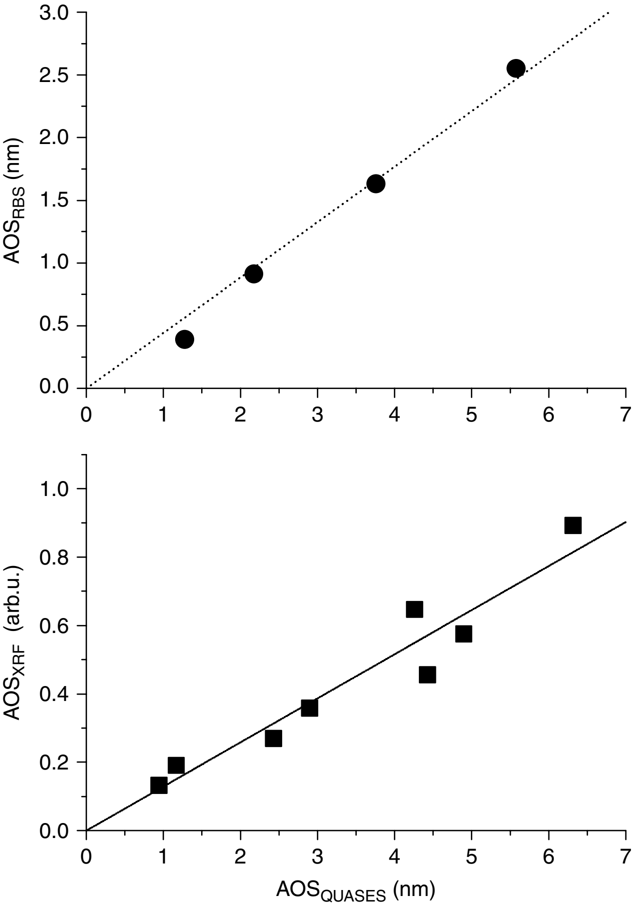

Figure 3. Comparison between the results for the amount of substance of Zn in the two sets of samples determined by XRF and RBS against the AOS determined by QUASES-XPS-peak shape analysis. Note that the consistency of the relative thicknesses is very good (from Reference 1).

substrate of the respective samples before film growth. These are expected to have similar roughness as the grown film.

Analysis of peaks from the substrate

The upper panel in Fig. 4 shows the results of the quantification for the two sets of samples using the intensities coming from the peaks of the substrate plotted against the AOS_{QUASES} result from peak shape analysis. While the results for the SiO_2 substrate show a similar scatter from the expected straight line as in Fig. 3, the scatter is considerably larger for the Al substrate. This might be due to shadowing effects between the islands of ZnO, as we know that the ZnO deposits grow with strong island formation.

Analysis of peaks from the overlayer film

The lower panel in Fig. 4 shows the quantification obtained using the intensities of the peak from the overlayer (using the data from ZnO as reference). The deviation from the results of peak shape analysis is in this case extremely large and in some cases (the omitted peaks) no structure at all could fit the measured angular variation of the peak intensities. The reason for this is likely to be the shadowing effects from neighboring islands as discussed above.

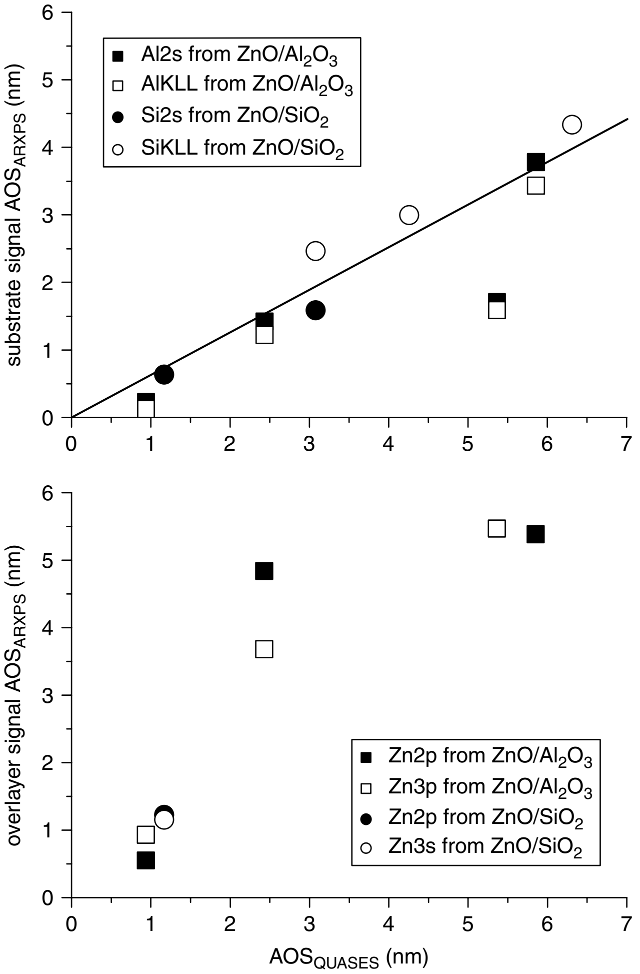

Figure 4. Comparison between the results for the amount of substance of Zn in the two sets of samples determined by ARXPS against the AOS determined by QUASES-XPS-peak shape analysis. The ARXPS analysis is based on the datasets after normalization to the rough substrates to reduce the effect of surface roughness. Note that the consistency of the relative thicknesses is much worse than in Fig. 3.

CONCLUSION

In conclusion, the ARXPS technique is very much dependent on surface roughness as well as on the morphology of the thin films. Thus, for reliable ARXPS analysis of nanometre thin films it is necessary to have independent knowledge on surface roughness as well as on the distribution of islands of the thin films. Without such knowledge, the uncertainty is very large.

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REFERENCES

1. Martin-Concepcion AI, Yubero F, Espinos JP, Garcia-Lopez J, Tougaard S. *Surf. Interface Anal.* 2003; **35**: 984.
2. Fadley CS, Baird RJ, Siekhaus W, Novakov T, Bergström SAL. *J. Electron Spectrosc. Relat. Phenom.* 1974; **4**: 93.

3. Seah MP, Smith G. *Surf. Interface Anal.* 1990; **15**: 751.
4. Holloway PH, Bussing TD. *Surf. Interface Anal.* 1992; **18**: 251.
5. Tyler BJ, Castner DG, Ratner BD. *Surf. Interface Anal.* 1989; **14**: 443.
6. Fulghum JE. *Surf. Interface Anal.* 1993; **20**: 161.
7. Cumpson PJ. *J. Electron Spectrosc. Relat. Phenom.* 1995; **73**: 25.
8. Werner WSM. *J. Electron Spectrosc. Relat. Phenom.* 1992; **59**: 275.
9. Nefedov VI. *J. Electron Spectrosc. Relat. Phenom.* 1999; **100**: 1.
10. Gunter PLJ, Niemantsverdriet JW. *Appl. Surf. Sci.* 1995; **89**: 69.
11. Kappen P, Reihs K, Seidel C, Voertz M, Fuchs H. *Surf. Sci.* 2000; **465**: 40.
12. Manuals for the QUASES-Tougaard and QUASES-ARXPS software packages can be downloaded at http://www.quases.com
13. Tougaard S. *J. Vac. Sci. Technol. A* 1996; **14**: 1415.
14. Tougaard S. *Surf. Interface Anal.* 1998; **26**: 249.
15. Martin-Concepcion AI, Yubero F, Espinos JP, Gonzalez-Elipe AR, Tougaard S. *J. Vac. Sci. Technol. A* 2003; **21**: 1393.
16. Tanuma S, Powell CJ, Penn DR. *Surf. Interface Anal.* 1993; **21**: 165.
17. Simonsen AC, Yubero F, Tougaard S. *Phys. Rev. B* 1997; **56**: 1612.