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Applied Surface Science 173 (2001) 134–139

applied  
surface science

www.elsevier.nl/locate/apsusc

## The estimation of the average dimensions of deposited clusters from XPS emission intensity ratios

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Received 27 June 2000; accepted 12 November 2000

### Abstract

We propose a method for the calculation of the average size of spherical clusters on a surface, using XPS emission intensity ratios. The method is applied to the case of Cu clusters on Dow Cyclotene 3022, a low permittivity polymer. It gives reasonable particle sizes and number densities, and shows that the clusters coalesce on annealing. TEM photomicrographs confirm the size and sphericity of the clusters formed. © 2001 Published by Elsevier Science B.V.

*Keywords:* Cluster formation; Metallization

There is a strong interest in nanometer-sized clusters. This is due, in part, to their expected quantum size effects in future photonic and quantum electronic devices [1–3]. It is also due, in part, to the fact that clusters are often associated with the initial stages of the thin film growth of metals, and the size and topography of these metallic clusters play important roles in the stability, adhesion and electronic properties of these films [4–6]. This latter aspect has been the subject of several reviews by Faupel and his colleagues [7–10].

An array of methods has been used to determine cluster dimensions. These include (a) direct methods (in which the clusters are actually imaged) such as TEM, STEM and SEM, (b) semidirect methods such as AFM, which present an image of the convolution of

the sample and probe tip [11–13] and (c) indirect methods such as grazing incidence X-ray diffraction [14–16].

Here, we present another indirect method, based on the change in the intensity ratio of two XPS peaks of the same element. Having different binding energies, they probe to different depths. Our method offers several advantages: (a) the data from previous XPS experiments, designed for other purposes, can be used, (b) it has high specificity and high surface sensitivity, and (c) it is independent of the extent of surface coverage. However, it is an approximation whose assumptions will be explored as they arise in the text.

We suppose that the clusters are distributed over the substrate surface and that they are spherical (direct methods [7–10] show that the clusters are, indeed, spherical, so that they can be represented by the single dimension,  $d$ , the diameter). The photoelectron signal intensity,  $I_i$ , of cluster  $i$ , having the diameter,  $d_i$ , may

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then be written as

$$I_i = I_i^0 \left[ 1 - \exp\left(-\frac{d_i}{\lambda_j}\right) \right] \quad (1)$$

where  $\lambda_j$  is the inelastic mean free path of the electron at that particular kinetic energy from the specific orbital  $j$ . For all the metallic clusters,

$$I = \sum I_i \quad (2)$$

(In fact, the exponential form of Eq. (1) is, itself, an approximation, albeit a very good one, and is universally used; its use has recently been reviewed [17].) Introducing the partial cluster coverage,  $\theta$ , the exponential equation then takes the form

$$I = I^0 \theta \left[ 1 - \exp\left(-\frac{d}{\lambda_j}\right) \right] \quad (3)$$

We further assume that  $d$  is the average of all the  $d_i$ . (The use of an average value of  $d$  is well-supported in the literature [9]. The inclusion of  $\theta$  has been validated in countless numbers of experiments in which the intensity has been shown to vary exponentially from partial coverage to many monolayers in thickness.)

Considering two XPS peaks from different orbitals of a given element, labeled 1 and 2, each with its own mean free path, we may take the ratio of two equations

of the form of Eq. (3) to obtain

$$R = \frac{I_1^0 [1 - \exp(-d/\lambda_1)]}{I_2^0 [1 - \exp(-d/\lambda_2)]} \quad (4)$$

The ratio,  $I_1^0/I_2^0$ , of the intensities of the two orbitals, is determined by using a very thick layer, where  $d \gg \lambda$ . This permits the determination of the average cluster size,  $d$ , from a knowledge of the  $\lambda$  values at each binding energy and the measurement of the intensity ratio,  $R$ .

We are presently studying the integration of Cu and Dow Cyclotene 3022 [18], a low permittivity polymer also known as BCB. We have used both photoacoustic FTIR and XPS to show that evaporated Cu deposits in the form of clusters. While we have discovered that Cu does not diffuse into the volume, even on prolonged annealing at 350°C, the clusters diffuse laterally to form larger clusters. We felt that clusters that grow on annealing, as well as on increasing the nominal thickness of the deposited layer, would offer an ideal test of our method. We compare the Cu 2p<sub>3/2</sub> ( $E_B = 932.5$  eV,  $\lambda = 13$  Å) and Cu 3d ( $E_B = 4$  eV,  $\lambda = 50$  Å) peaks. Their ratio,  $R$ , as a function of the nominal Cu thickness measured by our deposition meter, is found in Fig. 1, for an evaporation rate of 0.3 Å/sec.

These data were converted to average cluster sizes and are found in Fig. 2 as a function of nominal

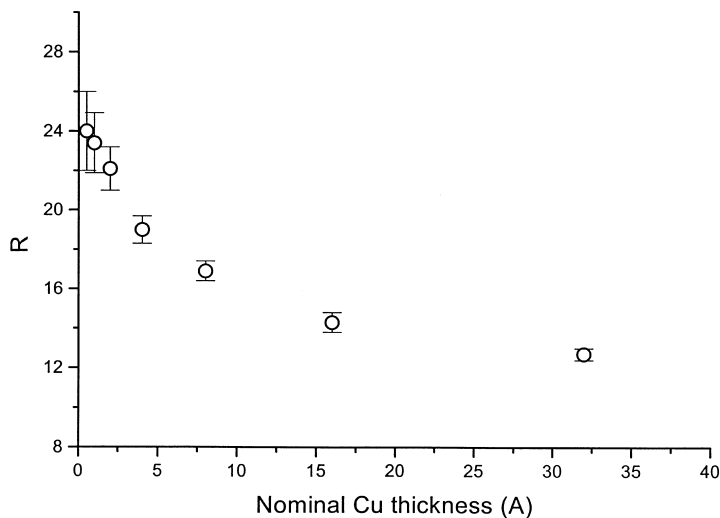


Fig. 1. The intensity ratio,  $R$ , as a function of the nominal thickness of evaporated Cu on untreated BCB.

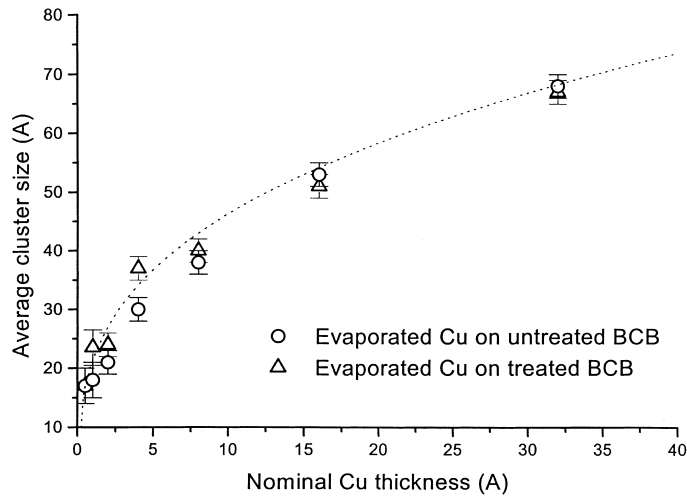


Fig. 2. The average size of Cu clusters as a function of the nominal thickness of evaporated Cu on BCB.

thickness. As an additional test, we have also plotted the Cu cluster size data obtained on Cyclotene surfaces previously treated by  $\text{Ar}^+$  beams. As will be shown in a subsequent publication, this treatment breaks Cyclotene bonds, causing a loss of aromaticity. These data fall on the same curve as do the data on the untreated surface, supporting our previous contention [18] that the poor adhesion of Cu to Cyclotene is due to weak interfacial interactions.

The total mass of all the spherical clusters is given by

$$\frac{4\pi d^3}{3} \frac{\rho N}{8} = \rho S t \quad (5)$$

where  $\rho$  is the bulk density of Cu,  $N$  the number of clusters in the area analyzed,  $S$ , and  $t$  the nominal thickness. On substituting  $n = N/S$ , we may write

$$d = \left( \frac{6}{n\pi} t \right)^{1/3} \quad (6)$$

The line in Fig. 2 satisfies the equation

$$d = 21.5t^{1/3} \quad (7)$$

that gives  $n = 1.92 \times 10^4$  clusters/ $\mu\text{m}^2$ .

We have calculated the cluster density as a function of nominal Cu thickness. The data, found in Fig. 3, show a rapid initial increase in cluster density before an almost equally rapid decrease to the steady-state value of  $1.92 \times 10^4$  clusters/ $\mu\text{m}^2$ , cited earlier. This

cluster density development is similar to that found by Faupel and his colleagues for Cu on polyimide [10]. In fact, we found that both cluster size and density are functions of deposition method, rate and annealing behavior.

As an example of the effect of annealing, we determined the average cluster size of a nominal 8 Å thick Cu layer, deposited at an evaporation rate of 0.3 Å/sec, as it was annealed at 350°C. The data, which are found in Fig. 4, show a rapid increase in cluster size which is over within 50 min. Fig. 4 also shows the change in the Cu  $2p_{3/2}/\text{C } 1s$  intensity ratio on annealing; this ratio reflects the screening provided by the growing Cu clusters. Again, the rapid change is over within 50 min.

XPS intensity ratios, covering several deposition variables of evaporated and sputtered Cu deposited onto both untreated and  $\text{Ar}^+$  treated Cyclotene 3022, have been used to derive the average diameters,  $d$ , of spherical Cu clusters forming on the Cyclotene surface under the various conditions used. Irrespective of conditions, the variation of the diameters as a function of thickness fit an equation of the form found in Eq. (6), leading one to conclude that (1) the particles remain spherical and (2) their number density stabilizes with increasing nominal thickness.

Previous data on other systems (see references [7–10] and the many references therein), as well as our own unpublished data on the Cu/Cyclotene system, show that the clusters are roughly spherical

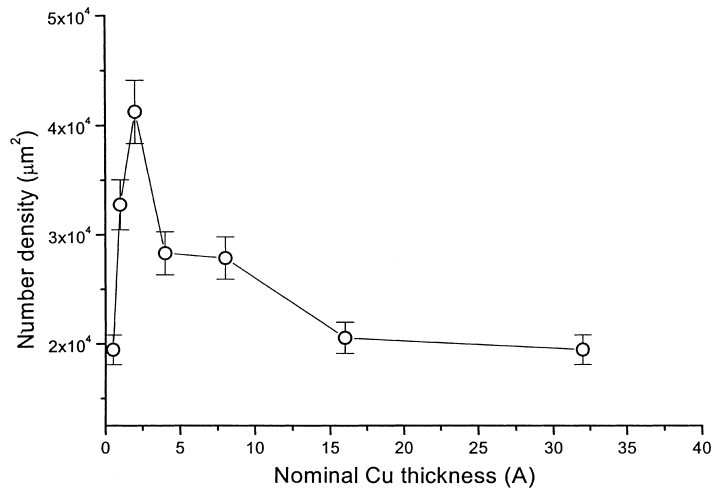


Fig. 3. The average density of Cu clusters as a function of the nominal thickness of evaporated Cu on untreated BCB.

although, some are contiguous. An example is seen in Fig. 5, part of a study to be presented in a subsequent article to deal with cluster deposition. Fig. 5, a TEM of 32 Å thick Cu on Cyclotene, annealed at 350°C for 15 min, reveals roughly spherical clusters 60–100 Å in size. Data similar to those in Fig. 4 (which is for 8 Å thick Cu on Cyclotene) reveals that clusters from 32 Å thick Cu on Cyclotene, deposited at 0.3 Å/s, should have diameters 80 Å in size. This is in good agreement with the value of 60–100 Å obtained by TEM. Our

method is also in good agreement with AFM data (images not shown). Table 1 shows a direct comparison of some of our XPS results with our TEM and AFM data.

In summary, a method has been developed for the use of XPS emission intensity ratios in determining the average diameters of spherical clusters deposited onto substrates. The values obtained are similar to those found using more direct methods, which also confirm the sphericity of the clusters. This technique is

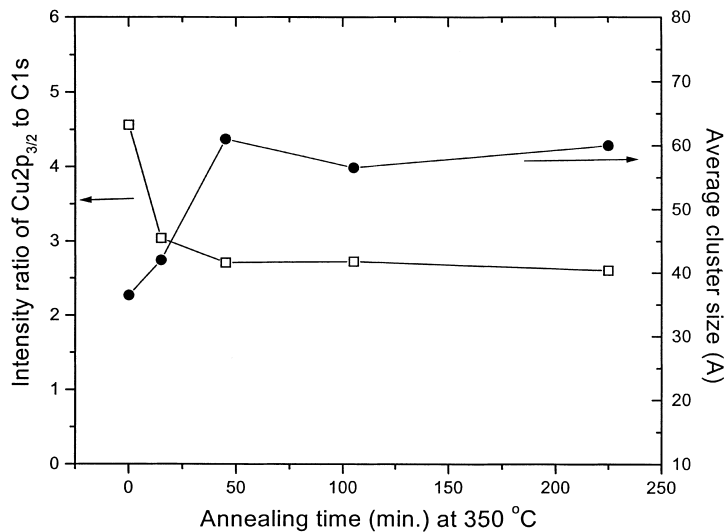


Fig. 4. The average size of Cu clusters and the Cu 2p<sub>3/2</sub>/C 1s intensity ratio as a function of annealing time at 350°C for 8 Å thick Cu.

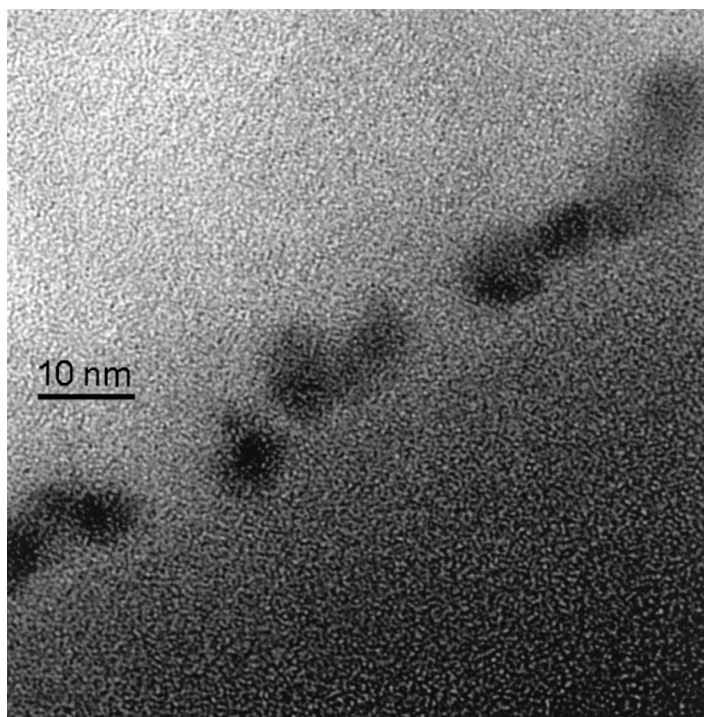


Fig. 5. A TEM photomicrograph of the interface formed by the evaporative deposition ( $0.3 \text{ \AA/s}$ ) of  $32 \text{ \AA}$  thick Cu, after annealing at  $350^\circ\text{C}$  for 15 min.

applicable to spherical clusters of any material formed on any substrate; Auger intensity ratios may be used instead of XPS intensity ratios.

### Addendum

During the final editing of this manuscript, our attention was called to the fact that Professor F. Faupel and his group, at Kiel, had also developed a method of determining cluster dimensions from intensity ratios.

Table 1

A comparison of estimated average sizes (in  $\text{\AA}$ ) determined by XPS, TEM and AFM for  $32 \text{ \AA}$  thick Cu on Cyclotene, annealed at  $350^\circ\text{C}$

Methods	As-deposited	Annealed at $350^\circ\text{C}$	
		15 min	45 min
TEM	50–100	60–100	
AFM <sup>a</sup>	75		180
XPS	67	80	$\geq 150$

<sup>a</sup> After removal of the effect of the tip.

Professor Faupel graciously furnished us a preprint of the article [19], where it was found that, aside from both groups using intensity ratios, the methods were different. We believe they complement each other.

### Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for funding this work. We also thank Ellen Griswold, Nortel Networks, Ottawa, for TEM measurements and for the permission to use Fig. 5.

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