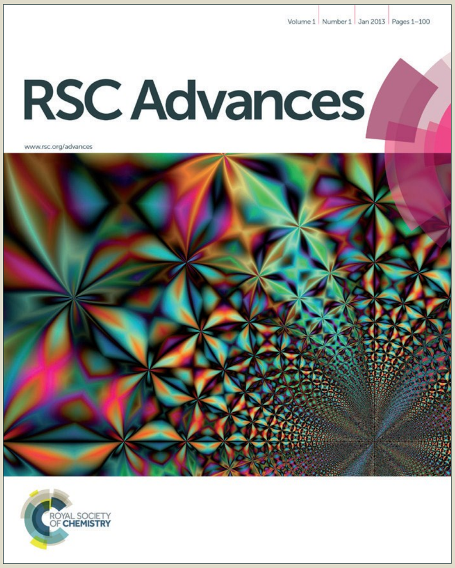
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Oxidation behaviour of Copper nanofractals produced by soft-landing of size-selected nanoclusters

Shyamal Mondal,[a†] **S. R. Bhattacharyya,**[a*]

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
First published on the web Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

We report the oxidation dynamics of Copper nanocluster assembled films, containing fractal islands, fabricated by nearly soft-landing of size-selected copper nanoclusters of average diameter of 3 nm. The time evolution of spontaneous oxidation in air of the prepared films at room temperature (RT) is studied. The compositional analyses of the films are carried out in an ultra-high vacuum (UHV) deposition chamber using an *in-situ* x-ray photoelectron spectroscopy (XPS) system. Morphological aspects of the deposited films are studied with high resolution scanning electron microscope (SEM) and atomic force microscope (AFM). We report spontaneous production of highly pure ($\sim 95\%$) technologically appealing nano-crystalline Cu_2O within 300 seconds of air exposure. Crystalline structure is probed by high resolution transmission electron microscopy (HRTEM) and the optical properties are studied using Cathodoluminescence (CL) attached in a SEM.

1 Introduction

Nanocluster deposition at very low energy (soft-landing) is a very powerful technique that gives the possibility of fabricating size controlled nano-islands or quantum dots[1–3] with predictable spatial distributions. This technique can also produce porous[4–6] and fractal[7,8] nanostructures with incredibly high surface to volume ratio. Owing to their potential applications in catalysis[9–12], efficient solar energy conversion[13,14], antimicrobial coatings[15–17], magnetic memory arrays[18] etc, studies of these type of nanostructures are very promising both from basic research and technological perspective. Copper is a material with high abundance in nature[19] and is a promising candidate to be used in most of the above mentioned fields. Moreover in nanocluster deposition by magnetron based gas aggregation type source, copper is one of the most suitable materials due to its high sputtering yield. Pure (bare) copper is very sensitive to oxidation when it is exposed to atmosphere and generally forms a mixture of two types of oxides, Cuprous(I) and Cupric(II), very quickly and in nanodimensional form the reaction rate will be much higher but the time scale of the phenomenon is not known in air or ambient condition. Though a few studies on oxidation of thin continuous metallic film[20,21] have been carried out, porous and fractal structures with very high surface to volume ratio are very complicated to be addressed and certainly deserve more attention.

In this work we study the oxidation dynamics of nanocluster assembled sub-monolayer metallic film, containing nanofractal islands of copper due to atmospheric exposure. Fractal islands are fabricated by nearly soft-landing of size-selected copper cluster on highly oriented pyrolytic graphite (HOPG). HOPG has been employed as substrate because firstly, it is chemically inert and secondly, soft-landed clusters get better mobility on its surface to diffuse and form larger aggregates (mostly fractals)[22]. Chemical composition of the as-grown as well as air-exposed fractal aggregates were investigated using an *in-situ* x-ray photoelectron spectroscopy (XPS) that exhibited spontaneous formation of pure Cu_2O nanocrystals within 300 s of exposure to ambient. Crystalline structure is confirmed by HRTEM analysis followed by CL study. Systematic XPS characterizations of the sample after different duration of air exposure give an idea about the time-scale of oxidation of copper nanofractals as well as giving the idea of stability of Cu_2O nanocrystals. As Cu_2O nanocrystal can be used as catalyst[23] this is a very crucial information. It also gives an experimental example for asymptotic behaviour[20] of time evolution of oxide growth in ultra thin and highly porous metallic film as fractal structures have very high surface area.

2 Experimental

Deposition of size-selected copper nanoclusters of an average diameter of 3 nm (or about 1100 Cu-atoms/cluster) at very low energy on HOPG substrate is performed using a state of the art ultra high vacuum compatible nanocluster source with subsequent mass selection process[3]. The used nanocluster source is a gas aggregation type source based on magnetron sputtering which is capable of producing ionized clusters with high flux

---

[a] *Surface Physics & Materials Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata-700064.*
∗ *Corresponding Author: satyar.bhattacharyya@saha.ac.in;*
† Present Address: Maharaja Manindra Chandra College, 20 Ramkanto Bose Street, Kolkata-700003; E-mail: smondal.xray@gmail.com

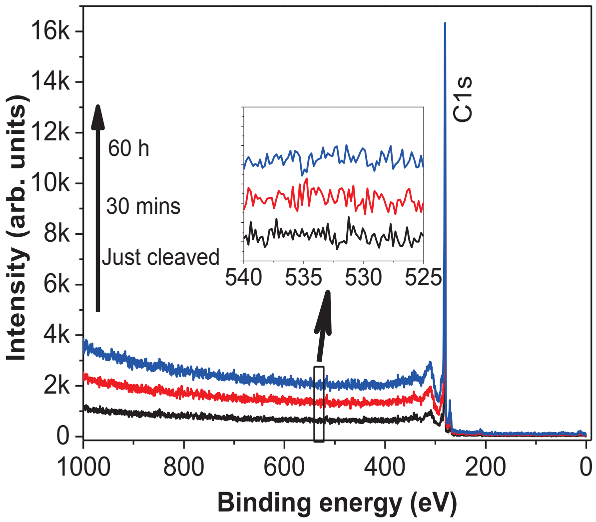


Fig. 1 XPS spectra from HOPG substrate after different atmospheric exposure. Data are represented in increasing order of time as indicated by the arrow. For BE range 540-525 eV high resolution spectra are shown (inset).

and a distribution of sizes. Produced clusters are carried only by the pressure gradient and after size selection get deposited on a substrate, very far from the source, attached in a large chamber. This arrangement ensures deposition at very low energy. It should be noted that QMF do not contribute to the kinetic energy of the clusters during size selection in the direction along the beam or the path of the clusters. The deposition system being equipped with an *in-situ* XPS facility provides the opportunity of chemically analyzing the deposited film (at pressure $< 5 \times 10^{-10}$ mbar) after deposition without exposing the sample to atmosphere or air. So just after deposition one set of XPS measurement was performed. The same sample was then taken out of the vacuum to laboratory atmosphere for a few different span of time and subsequent XPS measurements were carried out. The deposited material (Cu) starts to get oxidized when exposed to atmospheric condition and a gradual change in oxygen to copper ratio on the substrate (HOPG) surface occurs (discussed later quantitatively). Relative humidity of laboratory was maintained at 37-40% and the temperature was kept at 25°C during the whole experiment.

Deposition is carried out for 30 mins with 2 nA cluster current measured at quadrupole mass filter (QMF). Less than one microgram of copper is deposited in this process. So to detect appreciable change in oxygen to copper ratio in the sample, substrate should be chosen with extreme care, as oxidation of the substrate can complicate the conclusions on the oxidation of the desired material. Freshly cleaved HOPG is the best candidate in this respect as it remains unaffected for extended time of exposure to the atmosphere and that is ensured before starting the experiment. The XPS measurements were performed using $AlK\alpha$ (1486.6 eV) x-rays and the ejected photoelectrons were analysed by a Class150(VSW) hemispherical electron analyser at an operating pass energy of 20 eV and a scan rate of 0.15 eV/step with a dwell time of 1 second. We did our XPS measurements for $Cu2p$ and $O1s$ peaks keeping all other experimental conditions maintained same as before.Collected data were analyzed using commercially available CasaXPS software[24]. Our main goal is to identify the change in oxygen to copper ratio with exposure to atmosphere for different time spans. For this purpose we need a high signal to noise ratio. So, to increase the precision of measurement, we take 20 sweeps for each high resolution spectrum. Morphological aspects of the cluster assembled film are characterized with high resolution scanning electron microscope (SEM) and atomic force microscope (AFM). Crystalline property of the nanostructures is examined by high resolution transmission electron microscopy (HRTEM) of concurrently deposited copper nanoclusters on amorphous carbon film coated on a standard TEM

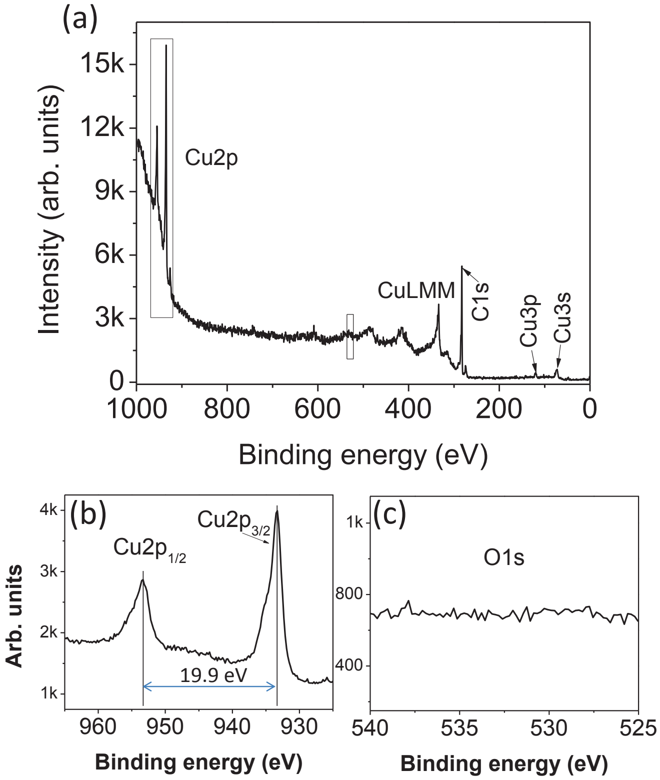


Fig. 2 (a) Survey spectra from the as deposited copper nanocluster film Cu2p and the position of O1s peak is indicated. (b) High resolution x-ray photoelectron spectra for $Cu2p$ showing the splitting between Cu2$p_{1/2}$ and Cu2$p_{3/2}$ equal to 19.9 eV. (c) A high resolution spectra from as deposited sample in the 540-525 eV energy range.

grid. CL measurements are performed by a Gatan CL system attached with the SEM by using 10 keV electron beam excitation. The details of the CL-SEM set-up can be found in reference[25].

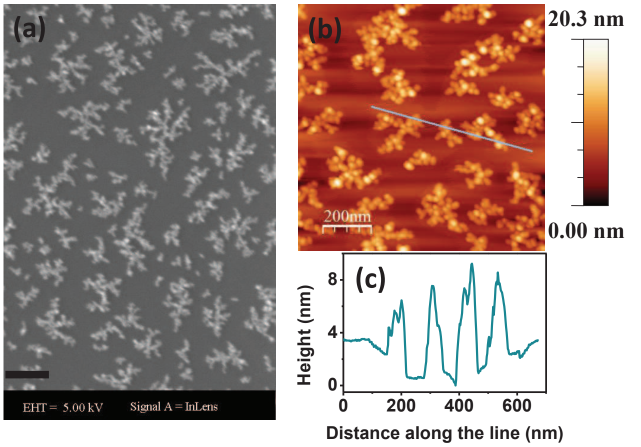


Fig. 3 (a) SEM image and (b) AFM image of nanocluster assembled film on HOPG substrate. (c) Height profile, along the line shown in (b), shows the features are of average 5-6 nm high (neglecting the uneven background). Black scale bar in the SEM image = 200 nm.

3 Results and discussions

As shown in the Figure 1, survey XPS spectra and high resolution spectra in the inset, no signal of any oxygen adsorption on HOPG substrate is detected even up to 60 h of exposure in the ambient which is much longer span than the longest exposure of the deposited film. This ensures very sensitive detection of oxygen adsorption on the intended metal structures. As-deposited sample is investigated first (without ambient exposure) to initialize the experiment. The survey spectra of the XPS measurement of as-deposited Cu-nanoclusters on HOPG is shown Fig. 2 (a). $Cu2p$ doublet peaks (at $\sim$ 953 eV and $\sim$933 eV), designated as $Cu2p_{1/2}$ and $Cu2p_{3/2}$ respectively, are shown in Figure 2 (b) after undergoing high resolution XPS analysis. We can clearly see from the high resolution spectrum in the energy range 540-525 eV [Fig. 2 (c)] that there is no signal of O1s present which confirms the fact that pure metallic fractals are formed and no oxidation took place during deposition. Also there is no other element which may contribute to oxygen adsorption is present.

SEM imaging gives 2D topographical information accurately in nanometers length scale but for out of plane or height information, AFM measurements are carried out. The results of SEM imaging and AFM measurements are shown in Figure 3. Coverage of the deposited film estimated from the SEM studies is $\sim$22%. Fractal islands are formed with fractal dimension $\sim$1.7 which is obtained using standard box counting method[26]. Fractal objects of finite volume contain quite larger surface area compared to a compact object[27] of same amount of material. Mechanism of fractal formation by nanocluster deposition has already been discussed in reported literature[7,8,28]. Nanoclusters, deposited at low energy, diffuse over substrate surface and on their encounter they either completely merge or just stick to each other giving rise to different final morphology. Merging or complete coalescence leads to formation of compact island structure[33,35] and just sticking together leads to ramified or fractal island formation. This merging and not merging of clusters or islands over the surface is governed by a ‘critical size of coalescence’,related to liquid-solid transition of clusters[36]. As observed from AFM measurements [Figure 3(b), (c)], average height of the fractal branches are $\sim$ 5 nm. It should be noted that the wavy nature seen in background of the AFM image is an artifact and so during height estimation these low height values were ignored. As the metallic nano-structures under study have large surface to volume ratio than other type of compact structures, they have more surface atoms. Hence very high rate of reaction is expected for such system in ambient oxygen pressure. In this situation, in order to detect oxidation in the deposited material, we need to examine the small changes in oxygen signal from sample in small temporal steps. It is achieved by proper choice of experimental condition such as substrate which does not get oxidized in much longer atmospheric exposure compared to the time scale of main experiment(discussed at the beginning of this section) and ultra high vacuum level. In Figure4(c) the oxygen peak ($O1s$: 540-525 eV range of binding energy) intensity is growing (with respect to the background signal) with increase in duration of air exposure. Merely looking at the oxygen peak it is impossible to infer the oxygen adsorption phenomenon quantitatively (due to many experimental reason photoelectron intensity can vary for different set of collections) and so the ratio of number of oxygen to copper atoms is calculated from XPS data for each step of oxidation. From the data base of CasaXPS and literature the it is found that relative sensitivity factor (RSF) of $Cu2p_{3/2}$ and $O1s$ peaks are 16.7 and 2.93 respectively for $AlK\alpha$ excitation. Using these values and the ratio of area under the curve of the high resolution $Cu2p_{3/2}$ and $O1s$ peaks after Tougaard type background subtraction[29], ratios of oxygen atoms to copper atom have been calculated. Figure 4(a) shows ratio of oxygen and copper atoms on the sample surface plotted against different times of atmospheric exposure. The growth of the ratio is entirely due to oxidation (oxygen adsorption) of deposited copper without any contribution from the substrate oxidation as was confirmed earlier in Fig. 1. Initially the rate of oxidation is high and within 300 s the O/Cu atomic ratio (r) assumes a saturation value. The data are fitted with a function (indicated by red line in the Figure 4(a)) of the form given as,

$$r = r_0[1 - exp(-bt)] \quad (1)$$

where r_0 should have the maximum value of 0.5 if only Cu_2O is formed and can have the maximum value of 1.0 if finally only CuO is formed, b is a constant which depends on the partial pressure of oxygen[30].

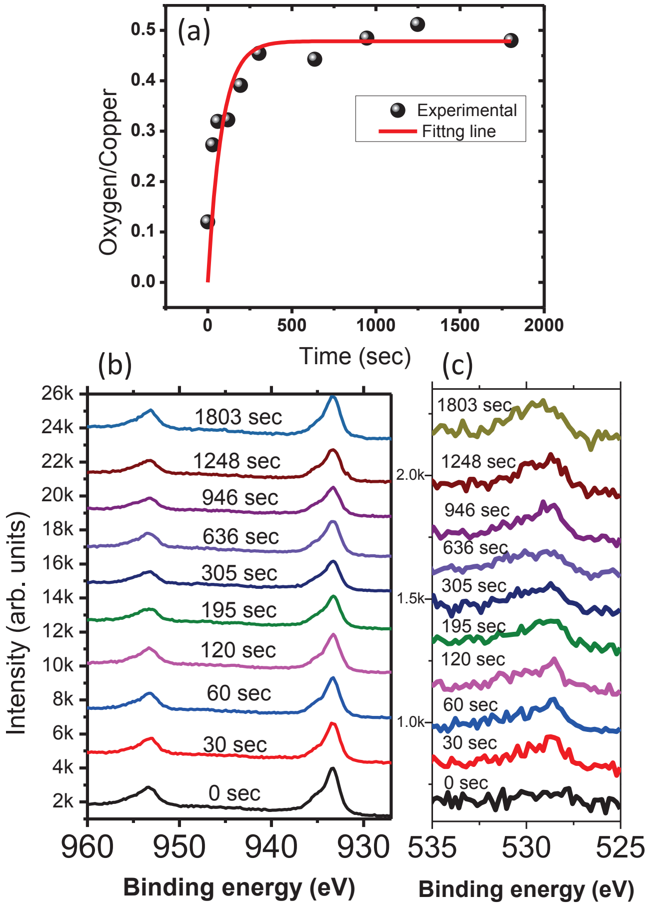


Fig. 4 (a) Atomic ratio variation with time length of atmospheric exposure. (b) High resolution x-ray photoelectron spectra for $Cu2p$. Spectra here show no satellite peaks between the two main peaks ($Cu2p_{1/2}$ and $Cu2p_{3/2}$). (c) High resolution spectra in 540-525 eV binding energy range collected from cluster assembled film after different air exposure time.

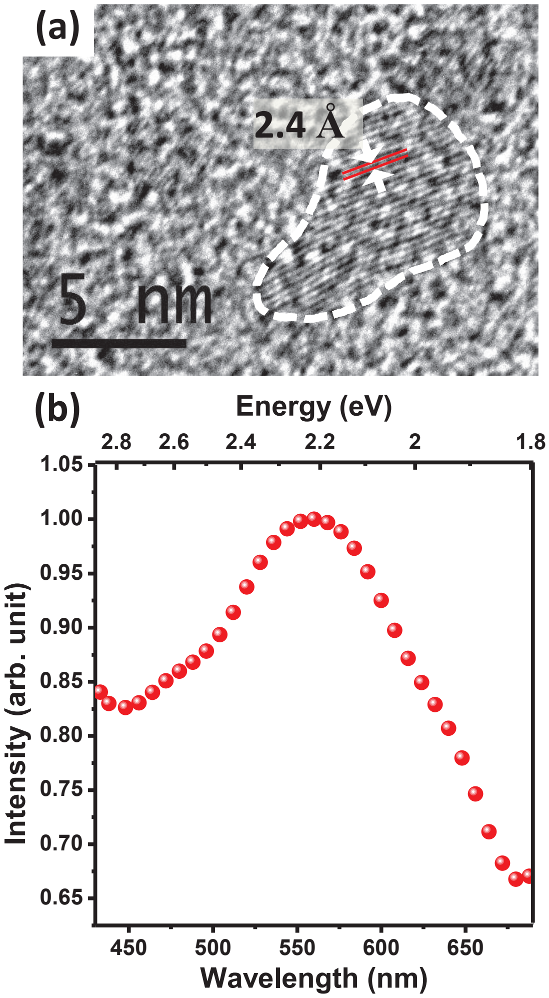


Fig. 5 (a) HRTEM image of deposited copper nanocluster amorphous carbon film showing lattice spacing of 2.4Å. (b) CL spectrum obtained from the deposited material on HOPG substrate.

From the fitted curve, the value of r_o is found to be ≈0.478 ±0.026, a value very near to 0.5 as obtained within 300 s of air exposure. So atleast in the probing depth of XPS study, all the Copper atoms in the fractal nanostructures are oxidized to Cu_2O and achieved saturation. Oxidation of metallic copper in presence of oxygen occurs through the formation of Cu_2O and CuO. Thermodynamically when partial pressure of oxygen is greater than the dissociation pressure for oxides, then only, oxides are formed. Kinetics of any chemical reaction depends on the trade off between change in free energy in the formation of different products in that reaction. Free energy change in the formations of Cu_2O and CuO are 122187 J/Mol and 99311 J/Mol respectively and from these values the oxygen dissociation pressure can be calculated as $\sim 10^{-17}$ and $\sim 10^{-13}$ in atmospheric pressure unit[31]. So if oxygen pressure is high enough ($> 10^{-13}$ atmospheric pressure), there is a high chance of CuO formation quickly after Cu_2O. But if oxygen pressure is lower than $\sim 10^{-13}$ but higher than $\sim 10^{-17}$ only Cu_2O can form. In the present case, oxidation of fractal structured nanoislands composed of copper nanoclusters in air, formation of only Cu_2O is observed and at least upto 30 mins it remained stable. From the HRXPS spectra of $Cu2p$, (fig. 4(b)), it is confirmed that no CuO is formed. Presence of

CuO generates shake up peaks in the observed range of binding energy in XPS data along with broadening of $Cu2p_{1/2}$ and $Cu2p_{3/2}$ peaks[32]. The oxide growth on the metallic non continuous film comprised of fractal nanostructures with branch height $\sim$ 5-6 nm cannot be explained by the theories applicable to continuous thick as well as thin films. This is because of the fact that nanofractals have much higher surface to volume ratio and hence much higher number of surface atoms. Moreover soft-landing of nanoclusters produces highly porous film[4]. In this scenario if we consider that the rate of formation of oxide molecules is directly proportional to the remaining unoxidised Cu atoms then, $dN/dt = b(N_0 - N)$. So the number of oxidized atoms (N) at an instant of time (t), is $N = N_0(1 - exp(-bt))$ when N_0 is the total number of Cu atoms in that volume. The atomic ratio of oxygen and copper for $\mathrm{Cu_2O}$ formation is $r = 0.5\frac{N}{N_0}$. Crystallinity of the nanostructures, produced by concurrent low energy cluster deposition on amorphous carbon film along with HOPG substrate, is examined by HRTEM. HRTEM image in Fig.5(a) shows lattice spacing of 2.4Å which corresponds to (111) interplaner spacing of Cu_2O. It should be noted that though for presentation purpose lattice fringe on only one nano-structure is zoomed in, all the nanostuctures gave fringes with same value of spacing.

Cathodoluminescence study [Figure5(b)] on the deposited film on HOPG substrate reveal a clear peak at ~560 nm wavelength which corresponds to energy of 2.21 eV. Bulk Cu_2O is a direct band gap semiconductor with band gap of 2.17 eV (570 nm wavelength) but we get a wider gap which is due the nanometer dimension of the nanocrystals. It must be noted that energy bands can only form in crystalline materials. Thus CL data support the TEM, XPS data that $\mathrm{Cu_2O}$ is formed.

4 Conclusions

In summary, the oxidation behavior of nanofractal structure, formed by soft-landed copper nanoclusters, is investigated in a time scale of second. Quick (<300 secs) formation of crystalline Cu_2O with very high production yield($\sim$ 95%) is observed just by atmospheric exposure in the laboratory. In cathodoluminescence spectra signature of band gap widening is detected due the nanometer dimension of the Cu_2O crystals unlike our previous investigation where formed islands were 3 dimensionally large[33]. The studies presented in this paper will help to gain better information on the time scale of oxidation of Cu which is important both technologically and fundamentally. Cu_2O crystal in nanometer size is a technologically promising material[23,34] and it can be obtained in pure form just by oxidation in atmosphere and it remains stable for more than 30 minutes in ambient.

5 Acknowledgement

Authors are grateful to Prof. Tapas K Chini, Dr. P. Das and Mr. Achyut Maity for SEM and CL studies, to Dr. B. Satpati for TEM study, to Prof. D. Ghose and Mrs. D. Chowdhury for AFM measurement and finally to Mr. Debraj Dey for technical help for the maintenance of the nanocluster deposition and XPS facilities.

References

1 N. Grönhagen, T. T. Järvi, N. Miroslawski, H. Hövel, M. Moseler,Decay Kinetics of Cluster-beam-deposited Metal Particles, *J. Phys. Chem. C* 2012, 116, 19327–19334

2 S. Mondal, B. Satpati, and S. R. Bhattacharyya, Formation of Monodispersed Films from Size-Selected Copper Nanoclusters, *J. Nanosci. & Nanotechnol.***2015**, 15, 611–615 (also: arXiv preprint arXiv:1307.0427, 2013).

3 S. Mondal, S. R. Bhattacharyya, Performance of a size-selected nanocluster deposition facility and in situ characterization of grown films by x-ray photoelectron spectroscopy, *Rev. Sci. Instrum.* 2014, **85**, 065109(1–9)

4 G. Palasantzas, S. A. Koch, and J. Th. M. De Hosson, Growth front roughening of room-temperature deposited copper nanocluster films, *Appl. Phys. Lett.* 2002, **81**, 1089–1091

5 V. N. Popok, I. Barke, E.E.B. Campbell, K-H Meiwes-Broer, Cluster–surface interaction: From soft landing to implantation, *Surf. Sci. Rep.* 2011, **66**, 347–377

6 C. Binns, Nanoclusters deposited on surfaces, *Surf. Sci. Rep.* 2001, **44**, 1–49

7 L. Bardotti, P. Jensen, A. Hoareau, M. Treilleux, B. Cabaud, Experimental observation of fast diffusion of large antimony clusters on graphite surfaces, *Phys. Rev. Lett.* 1995, **74**, 4694–4697

8 P. Jensen, Growth of nanostructures by cluster deposition: Experiments and simple models, *Rev. Mod. Phys.* 1999, **71**, 1695–1735

9 T. Ressler, B. L. Kniep, I. Kasatkin, and R. Schlogl, The microstructure of copper zinc oxide catalysts: bridging the materials gap, *Angewandte Chemie International Edition* 2005, **44**, 4704–4707.

10 A. Murugadoss, E. Sorek, and M. Asscher,Structure and Composition of Au–Cu and Pd–Cu Bimetallic Catalysts Affecting Acetylene Reactivity, *Top. Catal.* 2014, **57**, 1007–1014

11 M. B. Thathagar, and J. Beckers, and G. Rothenberg, Copper-catalyzed Suzuki cross-coupling using mixed nanocluster catalysts*J. Am. Chem. Soc.* 2002, **124**, 11858–11859

12 M. Nesselberger, M. Roefzaad, R. Fayal Hamou, P. Ulrich, Biedermann, F. F. Schweinberger, S. Kunz, K. Schloegl, G. K. H. Wiberg,S. Ashton, U. Heiz, K. J. J. Mayrhofer and Matthias Arenz, *Nat. Mater.* 2013, **12**, 919–924

13 H. M. Al Dosari and A. I. Ayesh, Nanocluster production for solar cell applications, *J. Appl. Phys.* 2013, **114**, 054305

14 César Clavero, (2014) Plasmonic conversion of solar energy. TBD. Lawrence Berkeley National Laboratory: Lawrence Berkeley National Laboratory. LBNL Paper LBNL-6249E.

15 N. Cioffi, L. Torsi, N. Ditaranto, G. Tantillo, L. Ghibelli, L. Sabbatini, T. Bleve-Zacheo, M. DAlessio, P. Giorgio Zambonin, and E. Traversa, Copper nanoparticle/polymer composites with antifungal and bacteriostatic properties, Chem. Mater., 2005, **17**, 5255–5262

16 M. S. Usman, M. E. E. Zowalaty, K. Shameli, N. Zainuddin, M. Salama,and N. A. Ibrahim, Synthesis, characterization, and antimicrobial properties of copper nanoparticles, *Int. J. Nanomed.*, 2013, **8**, 4467

17 A. Gupta and S. Silver, Silver as a biocide: Will resistance become a problem?, *Nat. Biotechnol.*, 1998, **16**, 888

18 S. Sun, Recent advances in chemical synthesis, self-assembly, and applications of FePt nanoparticles, *Advanced Materials*, 2006, **18**, 393–403

19 http://www.copper.org/

20 Kenneth. R. Lawless, The oxidation of metals, *Rep. Prog. Phys.*, 1974, **37**, 231–316

21 N. Cabrera, N. F. Mott, Theory of the oxidation of metals, *Rep. Prog. Phys.*, 1949, **12**, 163–184

22 K.A. Wepasnick, X. Li, T. Mangler, S. Noessner, C. Wolke, M. Grossmann, G. Gantefoer, D.H. Fairbrother and K.H. Bowen, Surface morphologies of size-selected Mo100±2.5 and (MoO3) 67±1.5 clusters soft-landed onto HOPG, *J. Phys. Chem. C*, 2011, **115**, 12299–12307

23 P. de Jongh, J. Kelly, Cu_2 O: a catalyst for the photochemical decomposition of water?, *Chem. Comm.*, 1999, **12**, 1069–1070

24 http://www.casaxps.com

25 P. Das, T. K. Chini, An advanced cathodoluminescence facility in a high-resolution scanning electron microscope for nanostructure characterization, *Curr. Sci.*, 2011, **101**, 849–854

26 R. Thouy, N. Olivi-Tran, and R. Julien, Fragmentation of two-dimensional mass fractals by surface-diffusion sintering, *Phys. Rev. B*, 1997, **56**, 5321– 5327

27 T. Tel, Fractals, multifractals, and thermodynamics, *Z. Naturforsch.*, 1988, **43a**, 1154–1174

28 P.Jensen, N. Combe,Understanding the growth of nanocluster films, *Computational Materials Science*, 2002, **24**, 78–87

29 M. P. Seah, Background subtraction: I. General behaviour of Tougaard-style backgrounds in AES and XPS, *Surf. Sci.*, 1999, **420**, 285–294

30 J. Kruger, H. T. Yolken, Room temperature oxidation of iron at low pressures, *Corrosion*, 1964, **20**, 29t–33t

31 C. H. Xu, C. H. Woo, and S. Q. Shi, The effects of oxidative environments on the synthesis of CuO nanowires on Cu substrates, *Superlattices and Microstructures*, 2004, **36**, 31–38

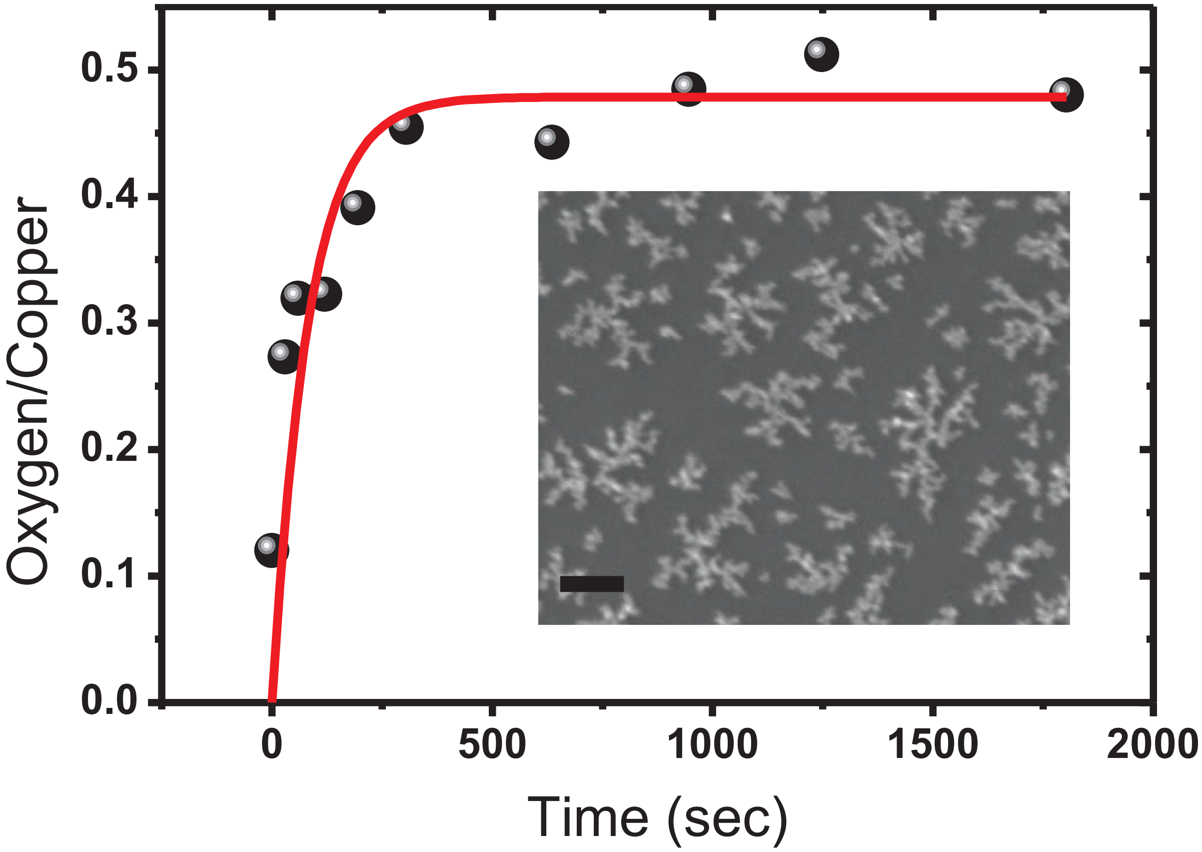
32 M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn, *Appl. Surf. Sci.*, 2010, **257**, 887–898

33 S. Mondal and S. R. Bhattacharyya, Morphological and optical properties of soft-landed supported nanoclusters: effect of rapid thermal annealing, *Appl. Phys. A*, 2014, **116**, 1621–1626

34 K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G. K. Paul, T. Sakurai, Thin film deposition of Cu_2O and application for solar cells, *Solar energy*, 2006, **80**, 715–722

35 G. M. Francis, and L. Kuipers, and J. R. A. Cleaver, and R. E. Palmer, Diffusion controlled growth of metallic nanoclusters at selected surface sites, *Journal of applied physics*, 1996, **79**, 2942–2947

36 P. Milani, S. Iannotta, Cluster beam synthesis of nanostructured materials, Springer Science & Business Media.


0.0
0.1
0.2
0.3
0.4
0.5
Oxygen/Copper
0
500
1000
1500
2000
Time (sec)