On the quest for a deterministic approach to plasma synthesis and conversion of nanowires

U. Cvelbar [1,2], G. Filipič[1] , O. Baranov[1,3], M. Košiček[1,2], and J. Zavašnik[1]

[1]*Jožef Stefan Institute, Ljubljana, Slovenia*
[2]*Jožef Stefan Postgraduate School, Ljubljana, Slovenia*
[3]*Plasma Laboratory, National Aerospace University "KhAI", Kharkov 61070, Ukraine*

Abstract: Building 1D nanostructures like nanowires is important for numerous applications. Plasmas present a great opportunity since nanowires in plasmas are produced not only faster but in bulk quantities with high quality. An extreme importance here is understanding of the basic mechanisms underlying growth of any type of metal oxide nanowire. Moreover, it is important to understand the mechanisms of growth in low-pressure and atmospheric-pressure plasmas in comparison to high-temperature but the thermally stable gaseous environment. Here we are on the quest for deterministic concepts of plasma synthesis for nanowire growth or even their subsequent conversion principles.

Keywords: nanowires, plasma synthesis, conversion

1. General

In the recent direction of research, plasmas are being used more and more for tailoring or synthesis of nanomaterials and advancing their properties, for example, to make them more efficient in catalysis or used as electrodes for water splitting.[1,2] Low-temperature plasmas have already proven to be a great source for the surface manipulations or supplying building blocks for nanomaterials and growth.[3] Similarly, such growths are also obtained at atmospheric pressure conditions, where impinging plasmas synthesise various types of nanostructures on surfaces.[4] Furthermore, the specific plasma-surface interactions are leading to synergistic effects, where very little is understood regarding basic processes taking place. To understand these processes at the atomic scale and mechanisms taking place, we implemented different low-pressure and atmospheric-pressure plasma treatments of nanoscale materials such as nanowires or nanoparticles. As results of interactions of various plasma species including ions, electrons or neutral atoms, the intrinsic properties of nanomaterials change as well as different nanostructures are grown on surfaces. These observations are supported by analytical methods in order to unravel what is occurring on the nanomaterial surface or bulk. Through the changes in the crystalline structure of a material, the growth of thin layers or reorganisation of its surfaces, the functionality of materials in applications such as gas sensing, liquid purification or similar, are significantly changed. The typical case of such 1D nanomaterial growth are nanowires of metal oxides.[5] Here in addition to growth in different plasmas and studying the role of plasma species, a comparison to thermally grown nanowires is done.[6] In some cases, the exhibited growth of nanowires grown at high-temperatures doesn't match nanowires grown in plasmas. Metal oxides seem to be the easiest nanowires to grow, however, sometimes subsequent conversions to nitrides or sulphides or even reduce oxide forms are needed. All these can be achieved by using various approaches utilising either plasmas or separated species created within and compared to neutral gas molecule interactions.

2. The case of copper-oxide nanowires

To highlight previously stated remarks, a case of plasma grown copper oxide nanowires is given, due to its difficulties in growth. The nanoscaled copper oxide is one

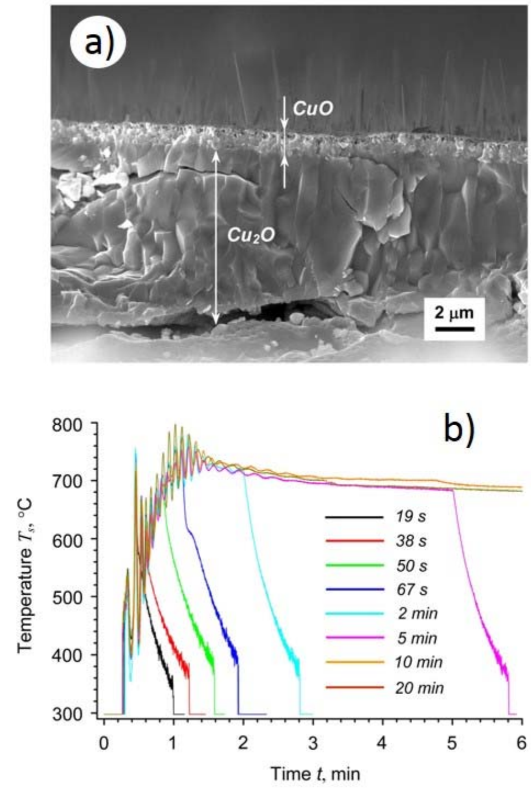

Fig. 1. a) SEM image showing the Cu_2O and CuO layers on Cu substrate oxidized in RF plasma discharge for t = 12 min; and (b) surface temperature versus processing time obtained by with time of growth as a parameter.

of the most demanded and perspective materials playing a pivotal role in many nanostructure-based emerging applications. Some unique electrical and mechanical properties of these new generation nanostructures are potentially able to boost the characteristics of sophisticated up-to-day devices. Nevertheless, a nontrivial technique commonly used for the synthesis of CuO/CuO_2 nanostructures (in particular nanowires), as well as very complicated growth and nucleation mechanisms, are their stumbling blocks significantly hindering the occupation of a relevant application niche. Here, we theoretically and experimentally demonstrate that the ultramodern plasma-based fabrication technique ensures avoiding highly

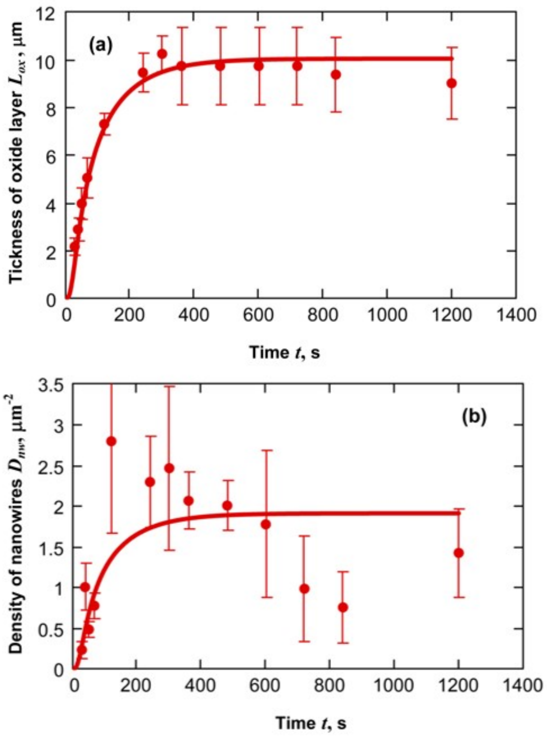

Fig. 2. Dependencies of the oxide layer thickness (Cu_2O + CuO) (a) and number density of nanowires (b) on the time: solid lines are the results of calculations from model, error bars correspond to the results of the experiment.

unfavourable, uncontrollable growth intrinsic to the commonly used thermal oxidation method. Moreover, it enables switching the process to a rapid, target-saturating mode leading to fast, highly controllable nucleation and growth of thin, long, densely packed, highly crystalline copper-oxide nanostructures directly on the copper surface, without involving any additional precursors and catalysts in the process. The developed multiscale numerical simulations reveal the basic mechanisms behind the target-saturating growth mode and the key control factors enabling highly predictable synthesis of dense oxide nanostructures of pre-determined size and surface density.

3. Results and Conclusions

The presented research unveils the fundamental aspects behind the plasma-supported growth of metal-oxide nanostructures and underlying oxide layers in the case of copper oxide nanowires.[7,8] Moreover, this is compared to the standard thermal growth of nanowires. The effect of plasma influence manifests in the fast growth of the oxide layers (tens of minutes) with a saturation of the oxide layer thickness with time. At that, the density of the ion current from plasma determines the saturation mode – the higher is the ion current, smaller is the thickness of the oxide layer at the fixed temperature of the growth. This behaviour differs greatly from the thermal growth of the nanostructures, where the parabolic law determines the dependence of the oxide layers and nanowires on time of the growth, with a typical growth time of about few hours.

By use of the developed advanced model[9,10,11], the obtained growth dynamics of Cu_2O and CuO oxide layers on copper exposed to an RF oxygen plasma discharge were investigated, and the mechanisms of growth were unveiled. According to the simulations results, the use of plasma affects greatly three parameters of the growth process, namely: i) a number of channels to deliver the copper atoms from the substrate to the growth area; ii) rate of the temperature increase at the substrate heating; and iii) the internal stress generation. The radiation defects generated at the ion bombardment are considered as the main reason for the saturation mode since the defects worsen the conditions for the short-circuit diffusion of the species necessary to grow the oxide layer. The growing density of the defects decreases the number of the channels through which the copper and oxygen are delivered to the growth areas on the oxide and inter-oxide surfaces at the short-circuit diffusion. Fast heating of the surface by use of plasma, in contrast to the slow heating by use of the thermal methods, results in enhancing the diffusion of the species involved into the reactions, and, hence, ensures the fast growth of the oxide layers. The internal stress generated at the oxide layer cannot be relieved at such fast growth, thus enhancing the rate of the growth by decreasing the energy of activation of the processes.

Since the density of NWs can be considered as a factor describing the production yield of the selected technology, the results allows considering the ion flux as a powerful tool to adjust the density of the NWs to a specified quantity by changing the density of the ion current in addition to the control of the sample temperature and gas pressure. The application of plasma can intensify the growth process and provides tailoring of the density of the NW arrays by selecting an appropriate value of the processing ion current.

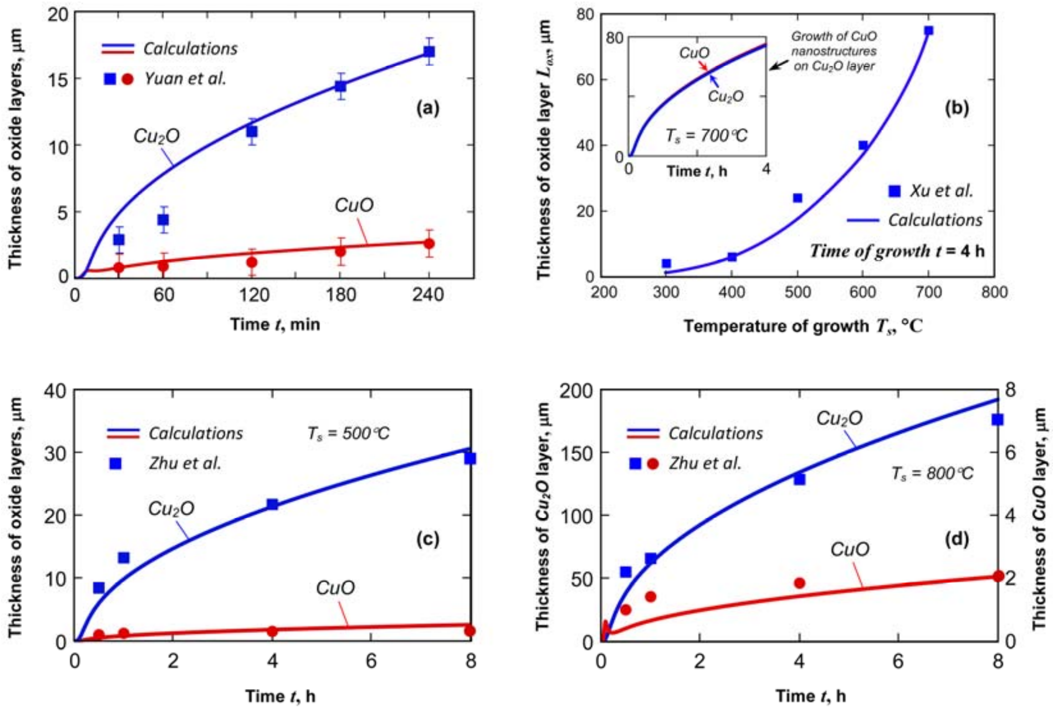

Fig. 3. Dependence of length of Cu_2O and CuO oxide layers on time for the thermal oxidation at 450 °C (after Yuan et al.[12]) (a); Total thickness of the oxide layer (Cu_2O + CuO) (after Xu et al.[13]) (b); Thickness of the oxide layers under atmospheric pressure at 500 °C (c) and 800 °C (after Zhu et al.[14])

Acknowledgments

Authors would like to acknowledge funding from Slovenian Research Agency (ARRS) programs P2-0082, P2-0056, and projects L2-7667 and Z2-8164.

4. References

[1] JS. Luo, L. Steier, MK. Son, M. Schreier, MT. Mayer, M Gratzel, Nano Letters, **16**, 1848 (2016).
[2] MA. Hassan, MA. Johar, A. Waseem, IV. Bagal, JS. Ha, SW. Ryu, Optics Express, **27**, A184 (2019)
[3] O. Baranov, I. Levchenko, JM. Bell, JWM. Lim, S. Huang, L. Xu, B. Wang, DUB. Aussems, S. Xu, K. Bazaka, Materials Horizons, **5**, (2018)
[4] A. Altaweel, T. Gries, S. Migot, P. Boulet, A. Mezin, T. Belmonte, Surface & Coating Technology, **305**, 254 (2016)
[5] Brittman, S.; Yoo, Y.; Dasgupta, N. P.; Kim, Si-in; Kim, B.; Yang, P. *Nano Lett.*, **14**, 4665–4670 (2014).
[6] Zhang, Q.; Zhang, K.; Xu, D.; Yang, G.; Huang, H.; Nie, F.; Liu, C.; Yang, S. Prog. Mater. Sci., 60, 208–337 (2014).
[7] Cheng, Q.; Yan, W.; Randeniya, L.; Zhang, F.; Ostrikov, K. J. Appl. Phys. **115**, 124310 (2014).
[8] Park H.; Lee, S.; Jo, M.; Park, S.; Kwon, K.; Shobana, M. K.; Choe, H. Journal of the Korean Ceramic Society, **54** (5), 438–442 (2017).
[9] O. Baranov, G. Filipic and U. Cvelbar, Plasma Sources Sci. Technol. (2018) accepted paper
[10] Filipič, G.; Baranov, O.; Mozetic, M.; Cvelbar, U. J. Appl. Phys. **117**, 043304 (2015).
[11] Filipič, G.; Baranov, O.; Mozetic, M.; Ostrikov, K.; Cvelbar, U. Phys. Plasmas **21**, 113506 (2014).
[12] Yuan, L.; Wang, Y.; Mema, R.; Zhou, G. Acta Mater., **59**, 2491–2500 (2011).
[13] Xu, C. H.; Wo, C. H.; Shi, S. Q. Formation of CuO Nanowires on Cu Foil. Chem. Phys. Lett. 399, 62–66 (2004).
[14] Y. Zhu, K. Mimura and M. Isshiki, Materials Transactions, **43** (9) 2173-2176 (2002).