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Formation mechanism of noble metal nanoparticles in reactively sputtered TiO₂ films

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Recently a simple recipe has been developed to prepare Ag nanoparticles in a TiO₂ matrix {Okumu *et al.*, [J. Appl. Phys. **97**, 094305 (2005)] and Dahmen *et al.*, [Appl. Phys. Lett. **88**, 011923 (2006)]}. In this scheme, silver nanoparticles are formed in a TiO₂ matrix by sputtering a thin silver film sandwiched between TiO₂ layers, followed by an annealing process. To determine the formation mechanism of noble metal nanoparticles in the TiO₂ matrix, we compare the behavior of Ag with two similar noble metals, gold and copper. The formation of metal nanoparticles in the TiO₂ matrix is investigated using a combination of techniques including x-ray diffraction, x-ray reflectance, and optical spectroscopy. Despite the similarity of the three noble metals, no nanoparticles are formed from Cu and Au. This is in striking contrast to the behavior observed for Ag. The difference can be explained by a three step process, which involves oxidation of the metal, dissociation of the metal oxide upon annealing, and metal aggregation to form nanoparticles. © 2010 American Institute of Physics. [doi:10.1063/1.3478710]

I. INTRODUCTION

Nanoparticles are of great scientific and technological interest. They form a bridge between bulk materials and molecular structures and often have properties that can be tuned by changing the particle size. This attribute is largely responsible for the great interest in employing nanoparticles in various industrial applications. To fully exploit their application potential it is mandatory to develop preparation techniques that can produce large amounts of nanoparticles with well controlled size at a competitive price.

We have recently developed a simple procedure which meets these requirements and is schematically depicted in Fig. 1.¹ In this procedure, Ag–TiO₂ nanocomposite films are prepared by the use of direct current (dc) magnetron sputtering. First, a TiO₂ layer of 30 nm thickness is reactively sputtered onto a glass substrate. This TiO₂ layer is amorphous as typical for this thickness and hence, no peaks are visible in grazing incidence (GI) x-ray diffraction (XRD) scans [see Fig. 1(a)]. Subsequently, a layer of 12 nm Ag is sputtered. This produces a thin continuous Ag film exhibiting peaks in the XRD measurement that are characteristic of Ag [Fig. 1(b)]. After sputtering an additional TiO₂ layer of 30 nm thicknesses under identical conditions as before, the Ag peaks are absent [Fig. 1(c)]. This surprising result indicates that the structural integrity of the Ag layer was destroyed during the sputter deposition of the second TiO₂ layer. However, after annealing the sample for 30–60 min at temperatures ranging from 300 to 500 °C, Ag diffraction peaks reappear in the XRD scans. This is due to the formation of crystalline Ag nanoparticles inside the TiO₂ matrix as confirmed by transmission electron microscopy.¹

Ag nanoparticles in TiO₂ have a number of interesting properties, which include photochromic behavior. Photo-

chromic materials reversibly change their color upon illumination at a specific wavelength. This effect has a number of possible applications that include information storage,² displays,³ smart windows,⁴ as well as switches.⁵ Photochromic materials consisting of a TiO₂ matrix with nanoscale metal particles have been recently of interest, in particular for the case of Ag–TiO₂.^{5–9} In this system, the photochromic effect arises from a spectral hole burning in the particle plasmon extinction band of the Ag nanoparticles.⁷

In recent years, several techniques have been developed

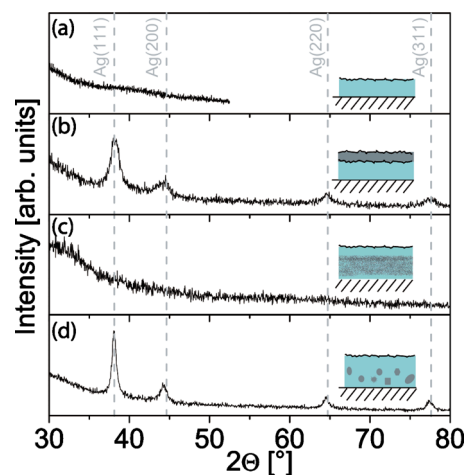


FIG. 1. (Color online) GI-XRD scans of an Ag–TiO₂ nanocomposite system at different stages of its fabrication process (see insets: dashed: substrate, light gray: TiO₂, darker gray: Ag). Ag diffraction peaks are labeled “Ag.” After reactive sputtering of 30 nm of amorphous TiO₂ onto a glass substrate (a) and 12 nm of Ag is sputtered. Ag XRD peaks show up in the spectrum as expected (b). Subsequently an additional layer of 30 nm TiO₂ is sputtered on top, after which the Ag diffraction peaks are absent (c). The absence of peaks at this stage indicates a destruction of the structural integrity of the Ag layer. Annealing the sample (here: 30 min at 300 °C) makes the peaks reappear (d), due to the formation of crystalline Ag nanoparticles inside the TiO₂ matrix.

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that can produce metal nanoparticles in TiO_2 . The procedure depicted in Fig. 1 has the important advantage that it can be easily adapted by the coating industry which already produces many millions of m^2 of coated glass substrates annually. Hence the equipment to produce huge amounts of glass coated with Ag nanoparticles is already available in industry. Therefore, it would be highly desirable to develop an atomistic understanding of the Ag nanoparticle formation process. To reach this goal we compare the behavior of Ag embedded in TiO_2 with two other noble metals, i.e., Cu and Au. This comparison answers the question if similar nanoparticles can also be formed from other noble metals such as Au and Cu.

Interestingly enough, we observe a very different behavior for Au and Cu as compared with Ag. These differences are presented in detail and are discussed and explained in the following.

II. EXPERIMENTAL PROCEDURES

The silver, copper, and gold TiO_2 nanocomposite films were deposited on glass and quartz substrates; this was followed by an annealing procedure. For all nanocomposites, first a 30 nm thin TiO_2 layer was deposited by reactively sputtering a Ti target at a constant pressure of 0.8 Pa and a constant discharge current of 900 mA in an oxygen/argon atmosphere. The metal films were then deposited on top under different conditions. In the case of silver and copper, 12 nm and 11 nm thick films, respectively, were deposited by sputtering a metallic target. In the case of gold, 14 nm thick films were deposited by thermal evaporation. For all cases, the layer stack was completed by depositing a second TiO_2 film via reactive dc magnetron sputtering under conditions identical to the deposition of the first TiO_2 layer. The purity of the films was ensured by evacuating the deposition system to a base pressure of approximately 2×10^{-6} mbar prior to each deposition process. The thicknesses of the films were confirmed by performing x-ray reflectometry (XRR) on corresponding single layer reference samples and on the complete layer stacks.

The fabricated films were further investigated utilizing GI-XRD and optical characterization methods to determine the crystal structure and optical properties. After characterization of the as-deposited specimen, the films were subsequently annealed in an argon atmosphere at various temperatures for 1 h once the final temperature had been reached after a constant heating ramp of $10^\circ\text{C}/\text{min}$. The above-mentioned thin film characterization methods have been applied after each annealing step to investigate the influence of temperature on film properties.

To determine the origin of the differences between Ag and the other two noble metals, a variety of double layer stacks has also been investigated. For these films, a silver layer has been deposited on silicon or glass substrates, respectively, in a metallic dc sputtering process, which was followed by subsequent deposition of a metal oxide via reactive sputtering.

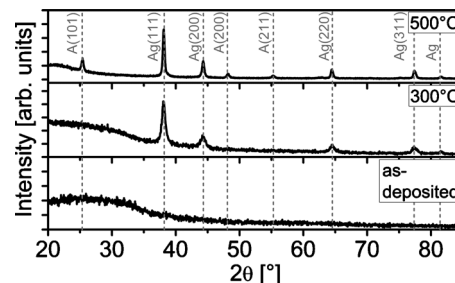


FIG. 2. GI-XRD scans of $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ -samples (30 nm/12 nm/30 nm), as-deposited (bottom), annealed at 300°C (center), and 500°C (top). Ag and anatase diffraction peaks are labeled “Ag” and “A,” respectively. In the as-deposited state, no peaks are visible. The TiO_2 thin films typically are only weakly crystalline at this film thickness. Hence, no peaks from the TiO_2 would be expected. Since clear silver peaks are visible in the as-deposited state before deposition of the top TiO_2 layer, the absence of any corresponding peaks in the three layer stack is clear evidence of a severe structural deterioration of the silver film during TiO_2 top layer deposition. Upon annealing silver peaks occur, indicating the presence of metallic crystalline silver in the layer system. At higher temperatures, also the anatase phase of TiO_2 is formed.

III. RESULTS AND DISCUSSION

As a reference, we will first discuss the results for the Ag– TiO_2 nanocomposite thin films. Figure 2 displays GI-XRD scans of these films in the as-prepared state and after annealing at 300°C and 500°C , respectively. Before the top TiO_2 layer is deposited, XRD patterns show a very pronounced crystalline Ag structure [see Fig. 1(b)], while the TiO_2 is typically x-ray-amorphous at this low thickness under the deposition conditions chosen here. However, upon deposition of the top TiO_2 layer, the silver peaks are absent (lower graph) and the film appears fully amorphous. This indicates that the structural integrity of the Ag layer has been destroyed by the deposition of the top TiO_2 layer. When this layer stack is subsequently annealed, Ag diffraction peaks reappear (see center and top graphs). In an earlier work¹ we have utilized transmission electron microscopy to show that annealing leads to the formation of Ag nanoparticles of various shapes and sizes inside the TiO_2 matrix. At this stage, the samples feature a broad extinction band in the visible and near infrared spectral regions because of the excitation of particle plasmons in these nanoparticles.^{1,7} The width of the inhomogeneously broadened extinction band increases as a function of initial silver film thickness, implying a broader distribution of nanoparticle sizes. In Fig. 1(d) we also notice that annealing the samples at 500°C leads to additional XRD peaks (as compared to annealing at 300°C) that can be assigned to the crystallization of TiO_2 in the anatase phase. The crystallization temperature found here is increased in comparison to pure TiO_2 films, which crystallize at 300°C . This behavior can be attributed to Ag atoms present in the TiO_2 matrix, which increase the activation barrier for crystallization of TiO_2 .

We now investigate the properties of the Au– TiO_2 nanocomposite films. Figure 3 shows GI-XRD scans of such a film in the as-deposited state and after several subsequent annealing steps, respectively. Probably the most striking difference in comparison to the Ag– TiO_2 films is that the film contains a crystalline Au structure at all stages, even in the

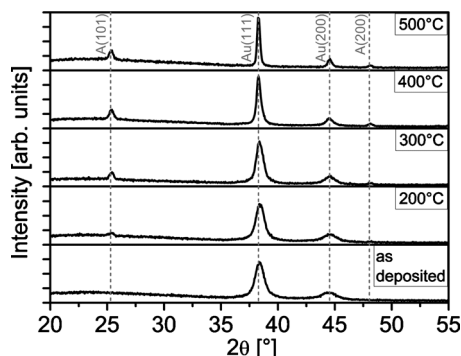


FIG. 3. GI-XRD scans for a Au-TiO₂ layer stack. In contrast to the TiO₂-Ag-TiO₂ system there are clear peaks indicating metallic gold already in the as-deposited layer stack. Upon annealing, the gold grain size increases with increasing temperature, as apparent from the decreasing width of the peaks. Also, the anatase phase of TiO₂ forms, as already observed for the silver system.

as-deposited state after deposition of the TiO₂ top layer. In contrast to the TiO₂-Ag-TiO₂ system, the Au film layer is not destroyed by the sputter deposition of the top layer of TiO₂. This is also confirmed by an XRR scan which is presented in Fig. 4. From the simulation of the measured XRR data it is evident that the structural integrity of the gold layer is not affected by the deposition of the top TiO₂ layer. By subsequent annealing, the structural quality of the gold layer is even improved further and the TiO₂ crystallizes into the anatase structure as already observed for Ag-TiO₂. Furthermore, optical investigations (not shown here) show no pronounced nanoparticle formation, in contrast to the Ag-TiO₂ system. This clearly shows that (i) the preparation of Au-TiO₂ nanocomposites with the desired properties is not possible with this fabrication technique and (ii) that the formation mechanism seems to involve material properties which are strikingly different for the Ag-TiO₂ system as compared to Au-TiO₂, since a fabrication method working well for the Ag-TiO₂ stack obviously fails in the latter case. This result is even more surprising since the formation of Au nanoparticles upon heating Au films has been reported by Fujisawa and co-workers.¹⁰ They have shown that deposition of gold films by thermal evaporation followed by a high-temperature annealing step leads to the formation of nanoparticles. Similar to our earlier work on Ag nanoparticles,¹ a

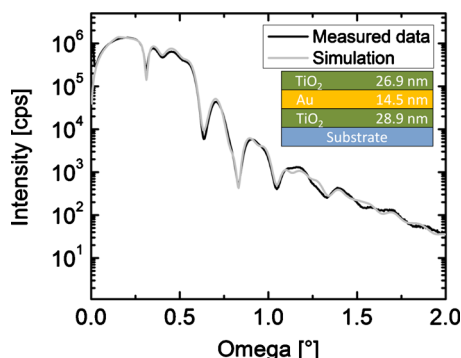


FIG. 4. (Color online) XRR measurement and simulation of a TiO₂-Au-TiO₂ film in the as-deposited state. The layer stack as deduced from the simulation clearly shows the integrity of the evaporated gold layer after deposition of the top TiO₂ film.

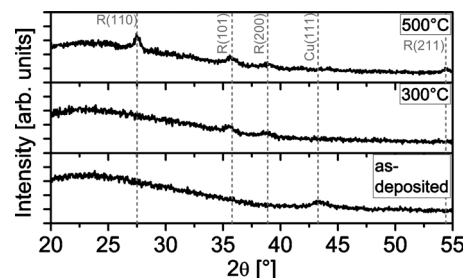


FIG. 5. GI-XRD scans of TiO₂-Cu-TiO₂ films annealed at various temperatures. Similar to the TiO₂-Au-TiO₂ system there is crystalline metallic copper apparent in the as-deposited layer stack. However, in contrast to both the silver and the gold system, the copper peak vanishes upon annealing, indicating a structural deterioration of the copper layer. Additionally the rutile phase of TiO₂ forms instead of the anatase phase.

correlation between the size of the gold particles and the initial Au layer thickness was found.¹⁰ The formation of gold nanoparticles by this different approach provides evidence that the distinct difference observed for Au-TiO₂ and Ag-TiO₂ layer stacks must be a feature inherent in our specific fabrication method.

To further elucidate the unexpected result for the Au-TiO₂ stack, we next present the results for the TiO₂-Cu-TiO₂ system after deposition and annealing at various temperatures. Figure 5 shows GI-XRD patterns of the films after the different stages of film treatment. The lower graph reveals a weak crystalline copper peak present in the as-deposited TiO₂-Cu-TiO₂ stack. However, the XRR scan and the corresponding simulation shown in Fig. 6 reveal that an oxide layer has formed on the copper film upon deposition of the top TiO₂ layer. Upon annealing, the Cu XRD peak disappears, in contrast to the finding for the Au-based stack. There is a second difference as compared to both the Ag-TiO₂ and the Au-TiO₂ films, which is that now the rutile phase of TiO₂ forms upon annealing, instead of the anatase structure that forms for the two other systems. It is assumed that upon annealing there is further oxidation of the copper layer, which would explain the disappearance of the copper peak for the annealed samples. Similar to the obser-

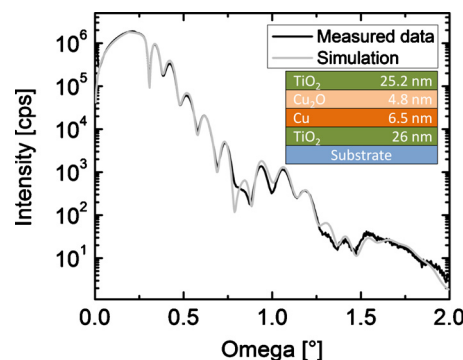


FIG. 6. (Color online) XRR measurements and simulation of a TiO₂-Cu-TiO₂ film in the as-prepared state. A reasonable simulation of the data could be achieved only by assuming the formation of a thin Cu₂O film upon reactive deposition of the top TiO₂ layer. The copper film was subjected to atomic oxygen for about 280 s during the deposition of the TiO₂ top layer.

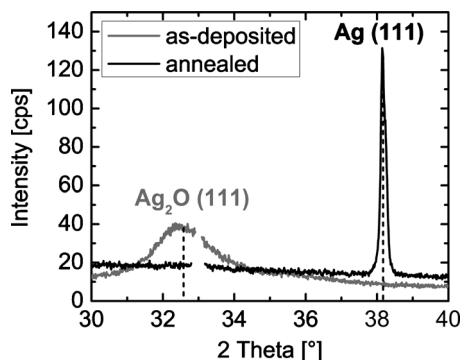


FIG. 7. Double layer system consisting of a 300 nm thick silver layer covered with a thin layer (~ 15 nm) of reactively sputtered Al_2O_3 . It is evident that in the as-deposited state no peak from metallic silver appears in the diffraction pattern. Instead, at around 32.5° a broad peak occurs which can be attributed to small Ag_2O grains. The Ag_2O lattice seems to be slightly strained, as evident from the small shift from the literature value of about 32.58° (Ref. 13). After annealing at 400°C for about 5 min a distinct silver peak appears while the Ag_2O peak has vanished. This indicates that the Ag phase has formed via dissociation of the oxide during the annealing procedure. A silicon (100) substrate has been utilized and the Si(211) peak at 33.05° has been removed from the graph.

valuations for the case of Au– TiO_2 , no pronounced plasmon resonance was found in any of the optical spectra investigated.

In an earlier work,¹ which dealt with the Ag– TiO_2 system only, it was concluded that the destruction of the crystalline Ag film was caused by the bombardment with negative oxygen ions which were created upon reactive sputtering of TiO_2 . It is well known that in reactive sputter deposition processes of metal oxides a significant number of oxygen ions are created at the target surface,¹¹ which are accelerated toward the growing film with energies often reaching the full cathode voltage.¹² It was argued that these ions strongly deteriorate the structural integrity of the thin silver layer, which would explain the absence of any Ag peaks in the XRD pattern. Upon annealing, structural reordering of the destroyed silver layer in the TiO_2 matrix leads to the formation of spherical nanoparticles to minimize the interfacial energy.

On the basis of this rather general mechanism, we would have expected very similar results for the Cu- and Au-based systems. However, it is evident from Figs. 3 and 5 that already in the as-deposited state a striking difference is found. Only the silver film structure fully disintegrates under the action of the bombardment with oxygen ions during the TiO_2 deposition process. This finding appears to be inconsistent with the oxygen ion bombardment model.

Therefore, it is necessary to refine the model of nanostructure formation to be able to explain the findings for the Au- and Cu-based systems as well. The different behavior of the Cu, Ag, and Au films implies that there is a specific difference for these three systems in their response to the bombardment by oxygen ions. The most likely scenario is the formation of an amorphous oxide in some of these systems. Proof for this hypothesis is presented in Fig. 7, which demonstrates that silver films can readily oxidize if subjected to a reactive sputter deposition process. A 300 nm thick silver film has been deposited onto a Si (100) substrate by sputtering from a metallic Ag target. This completely intrans-

parent metallic silver layer was subsequently covered by a thin Al_2O_3 film reactively sputtered from a metallic Al target. The deposition time for the Al_2O_3 thin film was only 150 s. During this very short period of time the silver film became completely transparent with a brownish color as typical for the Ag_2O phase of silver oxide. This finding provides evidence for the formation of an oxide. This is further supported by the XRD diffraction pattern displayed in Fig. 7, which shows a pronounced (111) peak of the Ag_2O phase. Apparently there is a significant shift in about -0.3° from the literature value, which indicates that the interlayer distance is slightly increased, probably as a result of mechanical stresses that formed during the oxidation of the original silver film. Moreover, upon annealing at approximately 400°C for about a minute, the film became highly reflective and exhibited a metallic appearance. The diffraction pattern reveals that the oxide peak has disappeared and is replaced by the (111) XRD peak of metallic silver with an fcc phase.

Similar experiments have been performed for a variety of silver film thicknesses (up to 500 nm) and different reactively sputtered metal oxides (HfO_2 and Ag_2O). Metallic silver films have also been treated with a low energy O^+ ion beam. In all three cases the silver films showed full oxidation in these processes and complete metallization upon subsequent annealing. Thick copper or gold films, in contrast, did not show any noticeable indication of oxidation when treated in the same manner. To understand this, we first discuss energetic considerations for the oxidation of the three metals Cu, Ag, and Au. The reaction



is characterized by a very small negative heat of formation of approximately -0.16 eV per Ag atom at room temperature. For the formation of Cu_2O the corresponding value is -0.87 eV per Cu atom. Finally, gold exhibits a slightly positive heat of formation. Hence it cannot oxidize under this condition. It is questionable if the small heat of formation for Ag_2O can explain the observation that even thick Ag films can be oxidized on a very short timescale. However, we need to consider that in the reactive sputter process, oxygen is available as an atomic species (negative oxygen ions). In this case, the reaction is



In this case the heat of formation is more negative by about 2.5 eV per Ag atom than for a reaction with molecular oxygen. Consequently, it is very likely that silver films are strongly oxidized in a reactive sputter atmosphere where many oxygen ions are available. On the other hand, the same consideration also holds for copper and gold.

However, besides the question whether or not the formation of an oxide is energetically favorable, also kinetic constraints need to be considered. Of particular importance is the growth speed of the oxide layer which is characterized by a power law¹⁴

$$\bar{x} = k_p \times t^{1/n}, \quad (3)$$

where \bar{x} is the oxide thickness, t is the reaction time, and k_p is a strongly material-dependent oxidation rate constant. For

copper it has been experimentally found that $n \approx 2$ and

$$k_{p,\text{Cu}} \approx 1.1 \times 10^{-9} \text{ m s}^{-1/2}, \quad (4)$$

at a sample temperature of 140 °C and an exposure to a constant atomic oxygen flux of 1.4×10^{17} atoms/cm² s.¹⁴ It was also shown that $k_{p,\text{Cu}}$ strongly increases with temperature and hence might be even smaller at sample temperatures of less than 100 °C, which are typical of the reactive sputter deposition of the TiO₂ top layers. For silver, experiments at room temperature yielded an almost linear rate law ($n \approx 1$) with

$$k_{p,\text{Ag}} \approx 3.5 \times 10^{-9} \text{ m s}^{-1} \quad (5)$$

for an exposure to a flux of 1.48×10^{17} atoms/cm² s of atomic oxygen.¹⁵ The linear nature of the oxidation rate law for silver has also been confirmed by our experiments (oxidation of thick silver films upon depositing Al₂O₃ and HfO₂ films).

To give an example of the very different oxidation speed of Ag and Cu, calculations yield that for an exposure of 100 s the above-mentioned rate laws correspond to an oxide layer thickness of 350 nm for Ag but only 11 nm for Cu, respectively. Hence, the significant difference in k_p and the power law (n) of Cu and Ag explains why Ag films completely oxidize while Cu films do not under similar conditions. On copper we have experimentally verified the growth of a thin oxide layer with a thickness of about 4.8 nm upon deposition of TiO₂. The difference between the measured copper oxide layer thickness (Fig. 6) and calculations using the rate laws from above is likely due to a difference in the flux of atomic oxygen (which is assumed to be smaller than 1.4×10^{17} atoms/cm² s in the reactive sputter process). Additionally, the growing TiO₂ layer may act as an additional barrier for oxygen diffusion into the underlying metal layer.

For gold no data has been found for the oxidation rate constant. This is presumably due to the fact that oxide formation in this case is energetically only favorable if sufficient amounts of atomic oxygen are available. Nonetheless, the comparison of the oxide formation on Ag and Cu surfaces strongly suggests that the large oxidation rate constant and the linear rate law of silver is the material property responsible for the significant differences observed between the Ag–TiO₂, Cu–TiO₂, and Au–TiO₂ nanocomposites.

The different growth rates for the different metal oxides can, in part, explain the significant difference between the different nanocomposites in the as-deposited state. However, oxidation of the noble metal alone is not sufficient to form metallic nanoparticles. A second step is necessary to form nanoparticles once the silver layer has been oxidized. This is the formation of metallic silver from the oxide upon annealing. This implies that at high temperatures the silver oxide has to be reduced to form metallic silver. The oxidation of Ag₂O and Cu₂O stops at 588 K and 1073 K, respectively, and is followed by oxide dissociation at 673 K and above 1173 K for Ag₂O and Cu₂O, respectively.^{16,17} These temperatures for Ag₂O are roughly in line with the annealing temperature of 573 K at which the nanoparticles were formed in the Ag–TiO₂ nanocomposite system.¹ For the Cu system this implies that even if the copper layer had been

oxidized in the reactive sputter process, no nanoparticles would have formed upon annealing below approximately 1173 K, which is in line with the experimental observation. Hence, in summary, the formation of metal nanoparticles in a TiO₂ matrix can be explained by a model where nanoparticles are formed by oxidation of metals, dissociation of the oxide upon annealing and aggregation of the metal particles to reduce surface energy.

IV. CONCLUSION

We have demonstrated that both copper and gold nanoparticles cannot be easily fabricated by sputter deposition. In order to fabricate nanoparticles using this technique, first, an oxide of the metal must be formed and second, the oxide dissociation must be accomplished within the available annealing temperature range. These findings have been used to propose a model to explain the mechanism of metal nanoparticle formation in metal oxides. The model is based on a three step procedure; oxidation of the metal upon reactive sputter deposition, oxide dissociation upon annealing and subsequent nanoparticle formation by aggregation. While the Cu₂O dissociation is impossible at the temperatures employed here, Au oxidation is too slow and unfavorable for the chosen process parameters. Only for Ag, parameters exist which are conducive to metal nanoparticle formation. This also implies that similar nanoparticles could be formed in other oxides as long as a sufficiently large number of oxygen atoms are available to oxidize the initial Ag film.

ACKNOWLEDGMENTS

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- ¹J. Okumu, C. Dahmen, A. N. Sprafke, M. Luysberg, G. von Plessen, and M. Wuttig, *J. Appl. Phys.* **97**, 094305 (2005).
- ²M. Lei, B. L. Yao, Y. Chen, Y. Han, C. M. Wang, Y. L. Wang, N. Menke, G. F. Chen, and M. G. Fan, *Proc. SPIE* **5060**, 28 (2003).
- ³J. N. Yao, K. Hashimoto, and A. Fujishima, *Nature (London)* **355**, 624 (1992).
- ⁴W. H. Armistead and S. D. Stookey, *Science* **144**, 150 (1964).
- ⁵M. Irie, *Chem. Rev.* **100**, 1685 (2000).
- ⁶Y. Ohko, T. Tatsuma, T. Fujii, K. Naoi, C. Niwa, Y. Kubota, and A. Fujishima, *Nature Mater.* **2**, 29 (2003).
- ⁷C. Dahmen, A. N. Sprafke, H. Dieker, M. Wuttig, and G. von Plessen, *Appl. Phys. Lett.* **88**, 011923 (2006).
- ⁸K. Naoi, Y. Ohko, and T. Tatsuma, *J. Am. Chem. Soc.* **126**, 3664 (2004).
- ⁹H. E. Chao, Y. U. Yun, H. U. Xingfang, and A. Larbot, *J. Eur. Ceram. Soc.* **23**, 1457 (2003).
- ¹⁰H. Fujisawa, Y. Morimoto, and M. Shimizu, *Jpn. J. Appl. Phys., Part 1* **45**, 7262 (2006).
- ¹¹J. M. Ngaruiya, O. Kappertz, S. H. Mohamed, and M. Wuttig, *Appl. Phys. Lett.* **85**, 748 (2004).
- ¹²S. Mráz and J. Schneider, *J. Appl. Phys.* **100**, 023503 (2006).
- ¹³Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, JCPDS, Card 76-1393, 1997.
- ¹⁴B. C. Gibson, J. R. Williams, A. T. Fromhold, M. J. Bozack, W. C. Neely, and A. F. Whitaker, *J. Chem. Phys.* **96**, 2318 (1992).
- ¹⁵D. L. Edwards, J. R. Williams, A. T. Fromhold, P. A. Barnes, J. P. Wey, W. C. Neely, and A. F. Whitaker, *Nucl. Instrum. Methods Phys. Res. B* **79**, 676 (1993).
- ¹⁶M. L. Zheludkevich, A. G. Gusakov, A. G. Voropaev, A. A. Vechev, E. N. Kozyrski, and S. A. Raspopov, *Oxid. Met.* **61**, 39 (2004).
- ¹⁷A. G. Gusakov, A. G. Voropaev, M. L. Zheludkevich, A. A. Vechev, and S. A. Raspopov, *Phys. Chem. Chem. Phys.* **1**, 5311 (1999).