Synthesis of Au microwires by selective oxidation of Au–W thin-film composition spreads

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Abstract

We report on the stress-induced growth of Au microwires out of a surrounding Au–W matrix by selective oxidation, in view of a possible application as ‘micro-Velcro’. The Au wires are extruded due to the high compressive stress in the tungsten oxide formed by oxidation of elemental W. The samples were fabricated as a thin-film materials library using combinatorial sputter deposition followed by thermal oxidation. Sizes and shapes of the Au microwires were investigated as a function of the W to Au ratio. The coherence length and stress state of the Au microwires were related to their shape and plastic deformation. Depending on the composition of the Au–W precursor, the oxidized samples showed regions with differently shaped Au microwires. The Au₄₈W₅₂ composition yielded wires with the maximum length to diameter ratio due to the high compressive stress in the tungsten oxide matrix. The values of wire length (35 µm) and diameter (2 µm) achieved at the Au₄₈W₅₂ composition are suitable for micro-Velcro applications.

Keywords: microwires, velcro, WO₃, Thin films, combinatorial materials science

1. Introduction

Two-dimensional micro- and nanosized objects like pillars, wires, rods and tubes can exhibit unique properties [1, 2] and are thus of interest for functional applications [3, 4]. One possible application of microwires and nanowires could be miniaturized Velcro for micro- and nanotechnology applications. Generally, Velcro consists of two parts with opposing surface structures. One part consists of a hook-like structured surface that allows for reversible connection to its counterpart having a loop-like surface. Several approaches were reported to realize microstructured artificial Velcro devices by using microelectromechanical system (MEMS) fabrication methodologies [5, 6]. For example, the anisotropic etching of Si was used to achieve mushroom-like surface structures [7, 8]. Another approach is to fabricate Si in a needle-like shape (‘black Si’) and to push these needles into the cavities between needles on the counterpart side [9]. A disadvantage of Si-based concepts is the brittleness of Si, which results in degeneration of the Velcro by breaking of its structures. This example illustrates the importance of the choice of materials for Velcro applications, especially with regard to the number of cycles that can be achieved. Further approaches to realize microwires involve microstructured polymers, electrodeposited wires [10], the use of templates [11, 12] and selective etching of wires that were grown out of a solidified eutectic within a surrounding matrix [13]. Introduction of certain defects into a carbon nanotube bend its end into a hook, allowing the development of nanosized Velcro [14]. Several of these
compressive stress in the thin film of the Cr was identified as the driving force for the high produced Bi nanowires out of a Cr–N matrix. The nitridation from soft metals (e.g. Sn, Cd, Zn) in an extrusion-like process, fabricating Velcro structures, is the formation of microwires [29, 30]. In thin-film samples, the formation of such wires was observed and was correlated to the high compressive stress within the thin film [25, 26]. This fabrication method for micro-/nanowires out of a thin-film precursor structure is promising because high stresses can be achieved in thin films. High thermal stresses originate from the different volume expansion of the film and underlying substrate during deposition and upon heat treatment. The stress state (compressive or tensile) as well as the amount of stress can be controlled by the deposition parameters and subsequent heat treatment, allowing adjustment of the wire growth and thus its properties.

The fabrication of wires by extrusion out of a thin film can be performed by using binary materials that have a limited solubility of their two elements. In this case, one element in the binary serves as the reservoir for the whisker growth and the other as the surrounding matrix out of which the whisker is growing. An important prerequisite therefore is that the matrix material has to undergo a large volume change to develop a high compressive stress within the thin film, giving rise to the extrusion and thus whisker formation of the other, rather soft element [27]. This high volume change can be achieved by post-deposition annealing where the matrix element is oxidized or nitrided. This was reported by Cheng et al who produced Bi nanowires out of a Cr–N matrix. The nitridation of the Cr was identified as the driving force for the high compressive stress in the thin film [28]. The formation of In whiskers by selective oxidation of Y out of a binary In–Y precursor structure was reported by Takahashi et al [29]. This was a first attempt at a comprehensive understanding of whisker formation dependent on composition and oxidation time using a combinatorial fabrication approach. However, as a material for mechanical applications like micro-Velcro, In has certain drawbacks, such as low Young’s modulus (E = 11 GPa) and melting temperature (157 °C). Further, the fast oxidation of In affects the wire growth and long-term stability.

This paper presents the synthesis of Au microwires by selective oxidation of W in a binary Au–W thin-film composition spread. Au was chosen because of its relatively high Young’s modulus of 78 GPa, excellent corrosion resistance and biocompatibility. The use of W as the matrix material is preferable due to the high Pilling–Bedworth ratio [30], giving rise to a large volume expansion on W oxidation. Furthermore, no stable intermetallic phases form between Au and W, ensuring that the maximum amount of Au is available for wire growth. To study the wire formation dependent on composition of the Au–W precursor, the thin-film composition spreads were fabricated by combinatorial deposition techniques and characterized by high-throughput methods. The combinatorial approach is advantageous for discovering new materials for wire extrusion from thin films, since a large number of samples are fabricated within one deposition process followed by efficient high-throughput characterization. This method provides a better understanding and allows faster optimization of materials as compared to conventional sample preparation [31, 32].

2. Experimental details

The Au–W precursor materials were fabricated as a thin-film continuous composition spread by using a co-deposition approach [33] in a combinatorial magnetron sputtering system (CMS 600/400LIN, DCA Finland). The system is equipped with five confocal magnetron sources arranged in a circular geometry (angle with respect to the substrate ∼45°, target to substrate distance ∼187 mm, figure 1(a)). The base pressure prior to all depositions was < 5 × 10⁻⁶ Pa. Four-inch Si (100) wafers with a 1.5 µm-thick thermal SiO₂ layer serving as a diffusion barrier were used as substrates. Pure Au (99.99%), W (99.99%) and Ar gas (6N) were used for thin-film depositions. The two elemental targets pointed confocally to the 4-inch Si substrate. The thin films were sputtered at a pressure of 0.66 Pa from elemental Au (22–66 W in radio frequency mode) and W sources (197–248 W in direct current mode). By varying the cathode angle and the deposition rates the composition range was adjusted from Au₃₄+W₇₆ (see inset in figure 1(b): number 19) to Au₁₇₁+W₇₃ (see inset in figure 1(b): number 1). Samples with a constant Au to W ratio were obtained in the direction perpendicular to this gradient. The deposition was carried out for 2800 s giving rise to a nominal film thickness of ~700 nm in the center of the wafer; the thickness increased to ~800 nm toward the wafer edge. The Au–W composition spread was cut into strips (width 5 mm) for subsequent heat treatments and characterization. The heat treatments were performed between 610 and 650 °C for 2, 4 and 8 h in an industrial furnace (Nabertherm S27, Germany) in laboratory air (30% humidity). The furnace was closed but not sealed after loading the sample. The humidity at the sample surface was not controlled and oxidation rates not measured. A reference strip was annealed in vacuum (CMS 600/400LIN, DCA Finland, SiC heater at pressure p < 5 × 10⁻⁶ Pa) to study the effect of oxygen on the microwire growth.

Surface and morphology investigations were carried out using a scanning electron microscope (SEM, JEOL 5800) operated at 20 kV. The chemical composition of the Au–W thin films was measured by energy dispersive x-ray spectroscopy (EDX), using an Oxford INCA system (Si:Li detector, working distance = 10 mm, 120 s counting time, error < 0.5 at.%). X-ray diffraction (XRD) measurements were performed with an X’Pert PRO MPD system (Cu Kₐ.
Figure 1. (a) Illustration of the combinatorial magnetron sputtering setup for the co-deposition of Au–W thin-film composition spreads. The Si substrate is located on a holder below the sputtering sources during deposition. Different colors on the substrate correlate to the variation in composition (W: blue, Au: red). (b) Au and W concentrations in a deposited sample measured by EDX along the line shown in the inset.

Figure 2. SEM micrographs showing a variety of Au microwire morphologies depending on the overall Au content. (a) Short and straight wires appear at 42 at.% Au. (b) With increasing Au content to 44 at.% the wires become longer and start bending. (c) They achieve a maximum length and a hook-like shape at 48 at.% Au. (d) False-color picture generated from elemental composition maps for 46 at.% Au (Au: yellow, W: blue).

radiation, spot size ~3 mm, PIXcel detector) to characterize the different phases, coherence length and stress state after annealing.

3. Results and discussion

After deposition, the Au–W strips containing similar compositional regions were annealed at different temperatures and for different durations in air to synthesize Au microwires by partial oxidation of the surrounding W matrix and investigate their shape and size. The annealing induces a large volume change via W oxidation and consequently a high compressive stress within the film. When the compressive stress reaches a critical value, the second phase, in this case Au, is extruded from the film. Different tungsten oxide phases were produced by varying annealing temperature and time. The heat treatment parameters resulting in the highest volume gain were identified as 610 °C and 2 h, and the compositional region yielding Au wires with the highest length to diameter ratio was determined. No further increase in the length to diameter ratio was observed when extending the annealing time beyond 2 h, whereas at higher annealing temperatures the wires acquired an undesirable Y shape.

To estimate the volume change of the W matrix by oxidation, the structures of the developing oxide phases have to be considered. Tungsten oxide phases exhibit high Pilling–Bedworth ratios \( R_{PB} \) [30], which can be calculated as \( R_{PB}(W \rightarrow WO_3) = 3.327 \); \( R_{PB}(W \rightarrow WO_2) = 2.049 \) and
Figure 3. XRD patterns for samples with an Au content ranging from 42 to 58 at.% along one strip, oxidized at 610 °C for 2 h: (a) 2θ range from 35° to 70°; (b) 2θ range from 70° to 115°. An increase of the peak intensities with Au (W) content is observed. Upon adequate heat treatment, the pure W oxidizes mainly into WO$_3$ with small amounts of WO$_2$ and W$_{11}$O$_{12}$, yielding the maximum volume increase on oxidation. The green stars denote diffraction peaks from the Si substrate.

$R_{PB}(W \rightarrow W_{11}O_{12}) = 1.919$ using the molar volumes of W ($9.544 \times 10^{-6}$ m$^3$ mol$^{-1}$), WO$_2$ ($1.956 \times 10^{-5}$ m$^3$ mol$^{-1}$) [34], WO$_3$ ($3.176 \times 10^{-5}$ m$^3$ mol$^{-1}$) [35] and W$_{11}$O$_{12}$ ($1.0077 \times 10^{-6}$ m$^3$ mol$^{-1}$) [36]. The corresponding volume changes are $\Delta V(W \rightarrow WO_3) \sim 233\%$, $\Delta V(W \rightarrow WO_2) \sim 105\%$ and $\Delta V(W \rightarrow W_{11}O_{12}) \sim 92\%$. X-ray diffraction experiments on the oxidized Au–W revealed the major WO$_3$ phase with only slight amounts of WO$_2$ and W$_{11}$O$_{12}$. The high volume gain was confirmed by the thickness increase from 240 nm to about 730 nm in a pure W film after oxidation at 610 °C for 2 h, which relates to a volume change of $\Delta V \sim 204\%$. The difference between the predicted and measured volume increase can be attributed to the small amount of WO$_2$ and W$_{11}$O$_{12}$ phases that expand less than WO$_3$. Therefore the thermal processing has to be adjusted to maximize the WO$_3$ phase that yields a maximum volume gain.

Figures 2(a)–(c) show the Au wires extruded out of the oxidized W–Au matrices of different compositions. The shape and especially length of the Au wires vary with Au content and amount of WO$_3$ produced by the annealing. Short and straight wires are formed at an Au content of 42 at.% (figure 2(a)). They become longer and start bending at 44 at.% Au (figure 2(b)). At an Au content of 48 at.% the wires have a length of about 35 µm and develop a hook-like shape at the end (figure 2(c)). For this composition the wire growth rate was estimated at 5 nm s$^{-1}$ from the ratio of the wire length and annealing time. To confirm that no W is present in the wires, a false-color picture of EDX composition mapping is shown in figure 2(d), where yellow corresponds to Au and blue to W. Besides the wires, this picture reveals small Au dots and additional surface features in the form of ‘blooming buds’.

XRD was employed for a further analysis of the structural changes in Au–W samples upon heat treatment. Figures 3(a) and (b) show the XRD patterns for different compositions, ranging from 42 to 58 at.% Au, for a strip annealed at 610 °C for 2 h in air. The diffraction patterns in the as-deposited state (not shown) indicate the presence of pure Au and W. The composition changes after oxidation to a tungsten oxide
matrix containing Au precipitates. The phases detected in these samples are WO$_2$, WO$_3$, W$_{11}$O$_{12}$, Au and Si from the substrate. Note that upon oxidation W mainly transformed into WO$_3$ with small additions of the WO$_2$ and the W$_{11}$O$_{12}$ phases. A polycrystalline microstructure without significant texture was observed in the as-deposited and annealed samples, allowing us to estimate the amounts of the different phases. No elemental W was detected after annealing. The XRD peak intensities follow the Au and W contents.

To characterize the stress state and wire formation, the coherence length and microstress in the Au precipitates were investigated and correlated to the developing surface morphology. The coherence length can be interpreted as a measure of the defect-free propagation of x-rays in the crystal lattice of Au extrusions. It is expected that the defect density in the crystal lattice of the Au wires increases due to the extrusion process, thereby reducing the coherence length. The high temperature during extrusion may heal some of these defects, and thus the coherence length can be interpreted as a measure of the grain size and the lateral dimensions of the Au wires. The coherence length and stress for each sample were investigated by fitting a Pearson VII function to the (220) and (222) Au diffraction peaks and using the approximation method [37]. Stress was calculated according to Hooke’s law by multiplying the microstrain and the Young modulus of Au.

In figures 4(a)–(c) the changes in surface morphology are shown by selected SEM images and a schematic, and are correlated to the coherence length and stress of the Au precipitates. The errors in the coherence length and stress decrease with increasing Au content, revealing clear dependences on the Au content. At the precursor composition Au$_{30}$W$_{70}$, the oxidized sample surface has a rough
morphology without any distinct features. The Au content is not high enough to allow extrusion of Au wires or agglomerates. Instead, small amounts of Au are extruded as little dots on the film surface. From Au41W66 to Au37W63 the increased amount of Au leads to surface cracks. The coherence length and stress of the Au precipitates do not vary significantly up to 41 at.% Au. Continuous Au agglomerates (‘blooming buds’) appear in Au42W68, along with an increase in coherence length and thus in lateral dimensions of Au precipitates. Further extrusion of Au out of the matrix reveals a strong decrease in microstress since the compressive stress of the tungsten oxide matrix does not affect the extruded Au features any more. From Au44W56 to Au47W53 the Au agglomerates change to wires and increase in length. Because of the increased volume of extruded Au, a further increase in coherence length and thus a stress reduction are observed. At higher Au contents, starting at Au47W53, additional Au is released out of the tungsten oxide matrix in the form of small dots next to the extruded wires (see figure 2(d)). From Au47W53 to Au50W47 the coherence length decreases because of the formation of small dots with decreased volume. The microstress within the Au precipitates increases due to the high density of small Au dots that are still partially located inside the tungsten oxide matrix and thus are affected by its high compressive stress. At Au53W47 the surface morphology changes from a mixture of wires and small dots to pillars. This is related to the reduced amount of tungsten oxide matrix compared to Au agglomerates. Thus, the large amount of Au mixtures with the leftover tungsten oxide matrix producing broad Au humps that are no longer shaped by extrusion. Although no wire growth is observed, the remaining tungsten oxide matrix still influences the Au agglomerates by providing a local minimum of coherence length at about 132 nm and by increasing the microstress up to 45 MPa. For Au contents >57 at.% the tungsten oxide matrix becomes discontinuous, which releases the compressive stress induced by the oxidation of W grains at Au interfaces. The Au precipitates between the tungsten oxide grains are therefore deformed but not extruded. Thus a steep decrease of microstress and an increase of coherence length at about 132 nm and by increasing the microstress up to 45 MPa. For Au contents >57 at.% the tungsten oxide matrix becomes discontinuous, which releases the compressive stress induced by the oxidation of W grains at Au interfaces. The Au precipitates between the tungsten oxide grains are therefore deformed but not extruded. Thus a steep decrease of microstress and an increase of coherence length are observed according to the growth in Au features. Summarizing these results, the growth of Au wires occurs only for compositions between Au47W53 and Au55W45. Especially the high coherence length and the low microstress within this composition range yield Au wires with low densities of defects and interfaces. The wires grown from Au48W52 have an average length of about 35 μm, a diameter of about 2 μm and hook-shaped ends, making this composition suitable for Velcro applications.

The results presented demonstrate the possibility of the growth of Au wires out of a W–Au matrix, where W is selectively oxidized by annealing, but does not react with Au. The driving force for the extrusion of Au wires is the large volume change due to the oxidation of W to WO3 generating a high compressive stress in the film. However, other parameters have to be considered for Velcro applications, such as the length and especially the radius of the Au wires R. The latter can be estimated from the ratio of the Au surface energy per unit area (γ) and strain energy per unit volume (ε) supplied by the surrounding tungsten oxide matrix [38]

$$R = \frac{2 \cdot \gamma}{\epsilon}.$$ 

As determined from SEM micrographs, the Au wires have a much larger diameter compared to In wires grown out of an yttrium oxide matrix. Further, the ε value is slightly larger for tungsten oxide than yttrium oxide due to the higher volume increase upon oxidation of W to WO3 than to Y2O3 and Y(OH)3 [29]. This relation should result in a decreased diameter of the Au wires, but since the surface energy of Au (1.506 J m−1) [39] is about twice as high as for In (0.7 J m−1) [40], the wire radius for Au turns out to be higher than for In. Considering this relation, the Au to W ratio with the highest strain energy per volume is identified around Au48W52, since the wires extruded at this composition exhibit the highest length-to-diameter ratio. Further, a maximum value in coherence length and a minimum value in stress state are determined for Au wires at the Au46W53 composition. In situ oxidation experiments in a controlled atmosphere (defined humidity and partial pressure of O2) would permit observation of the Au wire growth during the extrusion process and provide feedback for optimization of the wire length and diameter.

4. Conclusions

In this study, a combinatorial co-deposition approach was used to fabricate Au–W thin-film composition spreads as precursors for the formation of microwires by selective oxidation of the surrounding W matrix. The wire morphology strongly depends on the composition in the as-deposited state and correlates with the coherence length and microstress state of the Au precipitates. The results show the advantage of using W for selective oxidation due to the high Pilling–Bedworth ratio when W transforms into WO3. The Au46W52 composition yields the maximum compressive stress in the tungsten oxide matrix and wires with the maximum length to diameter ratio. These findings demonstrate the feasibility of co-deposited W–Au thin films as a precursor for the extrusion of Au wires by selective oxidation.

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