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Patterning thin metallic film via laser structured weakly bound template

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Abstract

A weakly bound buffer material is structured on a surface by interfering low power laser beams, as a template for patterning metallic thin films deposited on top. The excess buffer material and metal layer are subsequently removed by a second uniform laser pulse. This laser pre-structured buffer layer assisted patterning procedure is demonstrated for gold layer forming a grating on a single crystal Ru(1 0 0) under UHV conditions, using Xe as the buffer material. Millimeters long, submicron (0.65 μm) wide wires can be obtained using laser wavelength of 1.064 μm with sharp edges of less than 30 nm, as determined by AFM. This method provides an all-in-vacuum metallic film patterning procedure at the submicron range, with the potential to be developed down to the nanometer scale upon decreasing the patterning laser wavelength down to the UV range.

Keywords: Weakly bound buffer layer; LITD; Laser patterning

1. Introduction

The concept of laser induced thermal desorption (LITD) [1–6] is well established for the patterning of adsorbates on surfaces, and is widely used in basic surface phenomena studies such as diffusion [1–5]. For this application, however, it is limited for relatively weakly bound adsorbates. The high laser power (above 20 MW/cm^2, equivalent to 0.2 J/cm^2 for 10 ns duration of the laser pulse) typically needed for direct laser ablation of metallic films is often rather damaging for the substrate underneath, therefore such methods are rarely used for strongly bound metallic layer patterning.

In contrast, laser induced desorption of weakly bound buffer materials like Xe or water, requires relatively low power density (between 3 and 8 MW/cm^2 for Xe multilayer), conserving the quality and smoothness of the under laying surface. It is therefore possible to utilize laser ablation of weakly adsorbed buffer layers for the removal and patterning of metallic film deposited on top. This overcomes LITD limitations, and has enabled the patterning of metallic films and clusters on surfaces [7–9], and the in situ investigation of clusters surface diffusion [10]. Patterning Xe in the form of monolayer grating as a template for hydrogen sticking to silicon was reported earlier by Williams et al. [11]. Similarly, Zhao et al. used grating-like potassium profiles in order to direct the adsorption of CO due to different sticking probability at potassium covered and uncovered surfaces [12]. However both approaches are applicable only for the respective specific systems and cannot be used for the patterning of strongly interacting species such as metallic atoms or thin films [9].

In the present work, we describe a lift-off laser induced desorption method, aimed at patterning smooth metallic thin films that are millimeters long (the size of the laser beam) and submicron line width using a Nd:YAG laser wavelength of 1064 nm. A weakly bound buffer layer is laser-structured prior to deposition of the metal film, and serves as a template for the material to be deposited [13]. A second, uniform laser pulse is then used in order to eject

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and remove the excess buffer atoms and the undesired metal residue on top.

2. Results and discussion

The patterning procedure presented here is based on pulsed laser induced desorption that generates a metallic (gold) grating-like structure on a solid (Ru(1 0 0)) single crystal substrate, utilizing multilayer Xe as a weakly bound buffer material. The details of the experimental setup were described elsewhere [7,8,10]. The method is schematically shown in Fig. 1. Following a standard anneal and sputter cleaning procedure in ultra high vacuum, the sample is exposed to 99.999% pure Xe buffer gas at 20 K (Fig. 1(A)). A split (50%) p-polarized Nd:YAG laser pulse, 10 ns duration recombines and interferes on the ruthenium surface. This induces a sinusoidal temperature profile on the surface that leads to desorption of the buffer layer along the constructive interference troughs. A coverage grating is formed this way, as depicted in Fig. 1(B). This Xe multilayer grating was recently shown to stay stable up to its desorption temperature at 55 K [13]. A thin metallic layer of gold is then deposited (thermal evaporation, see Ref. [8]) on top of the structured buffer layer at a rate of 0.3 nm/min, as determined in situ by a quartz microbalance. The ablated Xe grating troughs are then filled-up with a smooth layer of metal (gold, 7 ± 2 nm thick), strongly attached to the substrate below. On the remaining areas covered by the buffer material, the metal film forms initially small 3D clusters on top of the Xe layer, as typical to metallic layer growth on buffer layers [14–18]. An intense second laser pulse is then employed uniformly over the entire sample surface in order to laser-desorb the remaining buffer material together with the undesired metal deposited on top. The patterned film deposited this way on the substrate (here Ru(1 0 0)) consists of smooth parallel metallic lines that are 5 mm long (the laser beam size). Their width in the range 3.25–0.65 μm, is determined by the laser power of the first (interfering) laser pulse. Finally, the sample is slowly heated at a rate of 1 K/s to 100 K, resulting in the slow desorption of residual buffer material that have not been completely laser-desorbed by the second laser pulse. The actual coverage grating formation is monitored in situ in the vacuum chamber by linear optical diffraction using a 5 mW He–Ne laser. The final sample structure is then imaged in air by AFM, at room temperature. The measurements were performed using AFM tapping mode with a TESP tip, using a DI 3100 Nanoscope instrument.

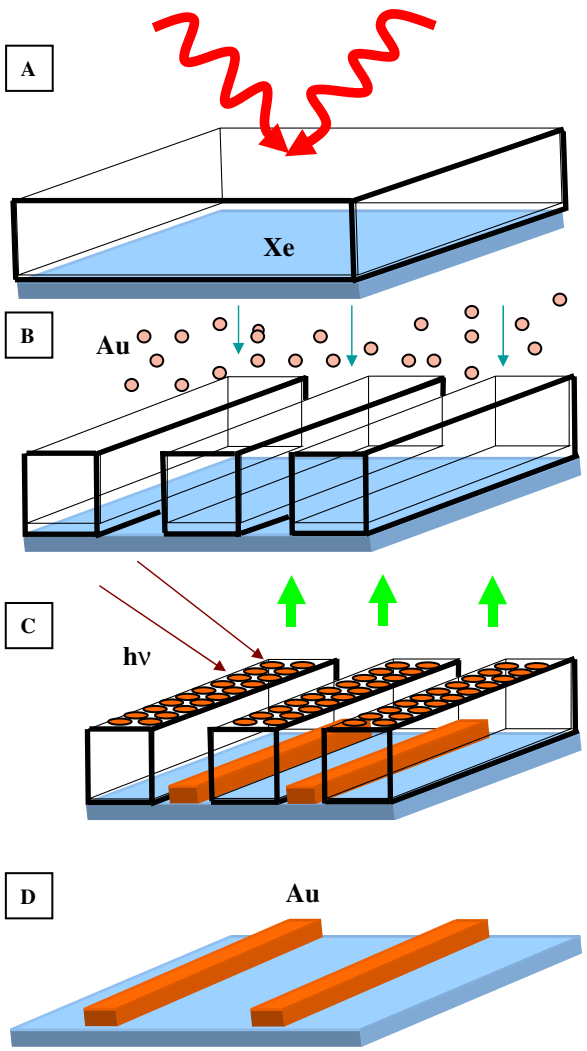

Fig. 1. A schematic view of the laser pre-structured, buffer assisted patterning process. After adsorption of the buffer layer on the substrate (A), it is spatially removed in a grating pattern by a desorbing laser pulse (lift-off) (B). Metal is then evaporated on the surface (C), followed by another laser pulse uniformly striking the entire sample surface. The final patterned metal remains strongly attached to the substrate (D).

AFM images of the gold grating patterns on top of Ru(1 0 0) are shown in Fig. 2. The laser power used for both the Xe grating formation (1.7–2.2 MW/cm^2 or 0.017–0.022 J/cm^2) and the second pulse (3–6 MW/cm^2 or 0.03–0.06 J/cm^2) are well below surface damage threshold [7,8,13].

The grating period (w) is dictated by the laser wavelength and by the angle of incidence (ϕ) between the two interfering laser beams according to Bragg equation ($w = \lambda/2\sin\phi$). For example, a laser wavelength $\lambda =$ 1064 nm and angle of incidence $\phi = 6.8 \pm 0.3°$ results in a grating period of 4.5 ± 0.3 μm, as shown in Fig. 2(A)–(C). Increasing the angle ϕ between the two recombining and interfering laser beams to 32° leads to 1.0 μm period, Fig. 2(D). The width of the grating troughs is determined by the laser power absorbed by the substrate. This is due to the exponential dependence of the buffer material desorption rate on substrate temperature. Therefore, higher first pulse power results in wider troughs of removed Xe and consequently wider metallic stripes will form. Such dependence of the width of gold lines on the power of the first (interfering) laser pulse is demonstrated in Fig. 2(A)–(C). The AFM images reveal 7 ± 1 nm high gold stripes (bright features in Fig. 2), performed using 120 ML Xe as the buffer material. The relative surface coverage of the gold stripes decreases from 72% (Fig. 2(A)), to 33%

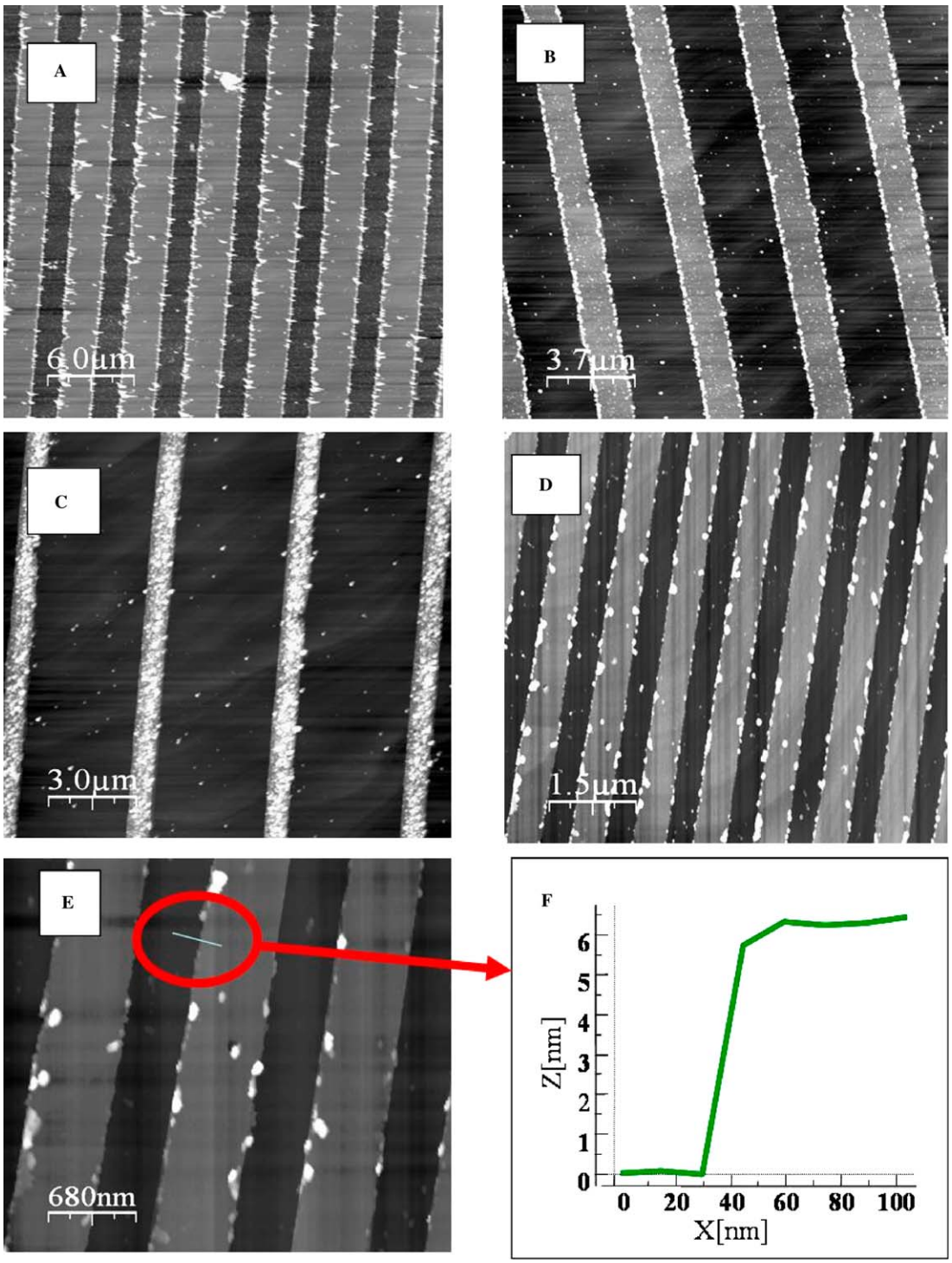

Fig. 2. AFM images measured in air of gold gratings (bright stripes) on a Ru(100) substrate performed via the laser pattering procedure: (A)–(C) 7 ± 1 nm high, 3.25 μm, 1.45 μm and 0.90 μm wide gold stripes in a period of 4.5 ± 0.2 μm (angle of incidence of 6.8°); (D) 6.5 nm high, 650 nm wide stripes in a period of 1.0 μm (angle of incidence of 32°); (E) zoomed area of 2D; (F) line-scan through a stripe in 2E above, demonstrating the sharp edges obtained.

(Fig. 2(B)) and to 19% (Fig. 2(C)) as the absorbed laser power density decreased from 2.2 to 1.7 MW/cm^2. The structure shown in Fig. 2(D) was obtained by employing an absorbed laser power of 2.5 MW/cm^2 that has generated 6.5 nm high gold stripes having a width of 650 nm within a period of 1.0 μm.

Metallic layers typically grow as 3D clusters on top of buffer materials [14–17]. A second laser pulse is, therefore, applied in the patterning procedure described above in order to remove the remaining buffer material along with the excess gold deposited on top. The features found within the ablated areas are small gold clusters that have not been

ejected to the vacuum by the second laser pulse, rather they landed on the substrate. The quality of the metallic grating pattern was found to be practically independent of the second laser power, above a threshold of 5 MW/cm^2. Nevertheless, large 3D metallic clusters appear at the edges of the gold stripes. The process of clusters deposition at the edges is schematically captured in Fig. 3(A). Steeper walls in the lift-off step of the buffer layer are expected to form at higher interfering laser power. However, the profile of the buffer material coverage modulation gradually changes with shallower Xe layer thickness at the boundary areas. Below a certain critical layer thickness, the buffer material does not satisfy the necessary conditions for pulsed metal ejection during the fast xenon desorption [7,8]. In these areas along the deposited stripes, 3D clusters more than 60 nm high form and stick to the smooth golden stripes deposited directly on the clean ruthenium substrate. Increasing the power of the second laser pulse, leads to higher density of clusters at the edges of the golden stripes, as shown in Fig. 3(B). This observation is not yet well understood. One possible explanation is that at high laser power, faster heating rate kinetically prevents recombination and aggregation of small clusters to form fewer but somewhat larger clusters.

It is interesting to examine the sharp edges that can be obtained along the metallic lines formed by the buffer layer laser-patterning technique. This defines the level of lateral resolution one may expects from this method. In Fig. 2(E) and (F), images of such edges are demonstrated using AFM tapping mode line-scan. Profiles that are 20 ± 5 nm wide at the edges are observed. Taking into account the AFM tip diameter one typically obtains sizes that include significant contribution to lateral dimensions from convolution of the AFM tip (a minimum of 15 nm diameter) which makes this number an upper limit for the actual edge profile width [18]. These are remarkably sharp edges considering that the wavelength used was 1064 nm. The ratio between the laser wavelength and the edge width suggests that by reducing the wavelength to 266 nm (fourth harmonic of the fundamental Nd:YAG) or to the wavelength of the operating excimer laser at the semiconductor industry −193 nm, one may expect reduction of edges width down to less than 5 nm.

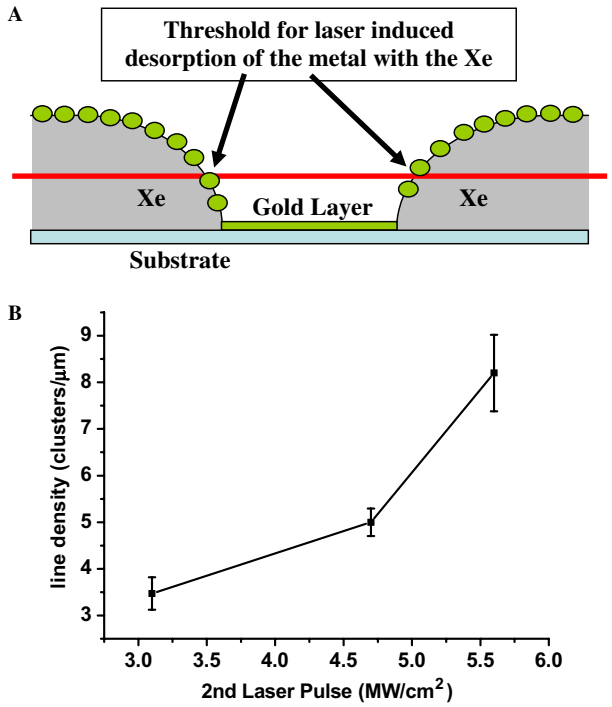

Fig. 3. (A) Scheme of the laser power threshold and buffer thickness necessary for cluster desorption/deposition at the metallic stripes edges. (B) The line-density of 3D clusters formed along the edges of the gold stripes is plotted against second pulse laser power. Clusters were 60 nm high on average.

3. Conclusions

A patterning procedure of a thin metallic (potentially also relevant to other materials) film has been introduced, by utilizing a lift off-like laser interference structuring of a weakly bound buffer material on a cold solid substrate. The structured layer is subsequently used as a template for selective deposition of the metallic thin films on the substrate. A second uniform laser pulse is then employed in order to remove the excess buffer material and the metal layer on top. The strongly attached metallic lines directly in contact with the substrate are not affected by the second laser pulse. The width of the smooth metallic stripes formed this way decrease with the interfering laser power, while their periodicity is determined by Bragg equation. This laser pre-structured (lift-off) buffer layer assisted patterning procedure is demonstrated in this study for 7 ± 1 nm thick gold layer forming a grating on a single crystal Ru(100) under UHV conditions, using Xe as the buffer material and imaged by tapping mode AFM. Millimeters long and submicron (0.65 μm) wide stripes (aspect ratio of 10^4) are obtained using an interfering laser wavelength of 1.064 μm with sharp edges of less than 20 nm. 3D clusters 60 ± 20 nm high are accumulated along the edges, their density can be partially controlled by the second laser pulse energy.

The all-in-vacuum clean patterning procedure described here is potentially effective with any kind of material that can be evaporated in vacuum be it a metal, semiconductor or an oxide film [20]. Moreover, it can be used for a wide range of light absorbing substrates such as solids, flexible polymers, etc.

This approach for patterning thin films has the potential to produce features that are less than 50 nm wide using conventional laser sources at 266 nm (fourth harmonic of a Nd:YAG laser) or by employing the industrial excimer laser source at 193 nm. The utilization of other buffer materials such as water [19] and carbon dioxide [21] have recently been demonstrated for the growth of metallic and oxide clusters. This is of practical importance allowing liquid nitrogen instead of liquid helium level of sample

cooling. Preliminary results of laser patterning on top of CO_2 as a buffer layer have already been demonstrated [8].

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References

[1] C.H. Mak, J.L. Brand, A.A. Deckert, S.M. George, J. Chem. Phys. 85 (1986) 1676.
[2] H. Mak, B.G. Koehler, J.L. Brand, S.M. George, J. Chem. Phys. 87 (1987) 2340.
[3] Z. Rosenzweig, M. Asscher, J. Chem. Phys. 96 (5) (1992) 4040.
[4] W. Zhao, R.W. Verhoef, M. Asscher, J. Chem. Phys. 107 (1997) 5554.
[5] D. Zhu, Th. Raising, Y.R. Shen, Phys. Rev. Lett. 61 (1988) 2883.
[6] T. Höche, R. Böhme, J.W. Gerloch, F. Frost, K. Zimmer, B. Rauschenbach, Nano Lett. 4 (5) (2004) 895.
[7] G. Kerner, M. Asscher, Surf. Sci. 557 (2004) 5.
[8] G. Kerner, M. Asscher, Nano Lett. 4 (2004) 1433.
[9] J.H. Weaver, V.N. Antonov, Surf. Sci. 557 (2004) 1.
[10] G. Kerner, Y. Horowitz, M. Asscher, J. Phys. Chem. B109 (2005) 4545.
[11] P.W. Williams, G.A. Reider, L.P. Li, U. Hüfer, T. Suzuki, T.F. Heinz, Phys. Rev. Lett. 79 (1997) 3459.
[12] W. Zhao, M. Asscher, Surf. Sci. 429 (1999) 1.
[13] G. Kerner, O. Stein, Y. Lilach, M. Asscher, Phys. Rev. B 71 (2005) 205414.
[14] L. Huang, S.J. Chey, J.H. Weaver, Phys. Rev. Lett. 80 (1998) 4095.
[15] V.N. Antonov, J.S. Palmer, A.S. Bhatti, J.H. Weaver, Phys. Rev. B 68 (2003) 205418.
[16] V.N. Antonov, J.H. Weaver, Surf. Sci. 526 (2003) 97.
[17] V.N. Antonov, J.S. Palmer, P.S. Waggoner, A.S. Bhatti, J.H. Weaver, Phys. Rev. B 70 (2004) 045406.
[18] Y. Ebenstein, E. Nahum, U. Banin, Nano Lett. 2 (2002) 945.
[19] E. Gross, Y. Horowitz, M. Asscher, Langmuir 21 (2005) 8892.
[20] D. Song, J. Hrbek, R. Osgood, Nano Lett. 5 (2005) 1327.
[21] P.S. Waggoner, J.S. Palmer, V.N. Antonov, J.H. Weaver, Surf. Sci. 596 (2005) 12.