1. Introduction

Laser-matter interaction has been the focus of intense research over the past three decades with diverse applications in the semiconductor industry (photolithography), sensing and analytical chemistry in general. Pulsed laser ablation of adsorbates under well controlled ultra high vacuum (UHV) conditions has enabled detection in the gas phase of large (mostly biologically important) molecules via mass spectrometry, but also to study the remaining species on the surface. In this chapter we will focus our report on these remaining atoms and molecules following selective laser ablation of weakly bound buffer layers as a novel tool for patterning of adsorbates on solid surfaces.

1.1 Patterning of adsorbates for diffusion measurements

Laser Induced Thermal Desorption (LITD) of adsorbates has developed as an important technique for surface diffusion measurements. In the hole-refilling method, a hole was burnt within an adsorbate covered surface. Subsequent time delayed laser pulse was employed to measure the refilling rate due to surface diffusion process (Brand et al., 1988, Brown et al., 1995). Accurate analysis of data acquired that way is not straight forward since the diffusion measured this way is two dimensional (and not necessarily isotropic). The actual hole size burnt into the surface is typically in the order of ~100µm, limiting the diffusion measurement to relatively fast occurring processes with low energy barrier compared to the activation energy for desorption.

A different method, utilizing two interfering laser beams to an adsorbate covered surface, has resulted in a sinusoidal spatial temperature profile and selective desorption of the adsorbates, thus creating a density modulation grating on the surface. In this way the typical measured diffusion length can decrease down to sub-micrometer scale.

The grating formed on the surface obeys Bragg law:

\[ w = \frac{\lambda}{2\sin(\theta)} \]  

(1)

\( w \) - grating period

\( \lambda \) - desorbing laser wave length
θ - angle between one of the incident laser beams and the surface normal. Such grating formation can be explored optically by recording a diffraction pattern from it. The decay of the measured 1st order diffraction due to smearing of the grating formation is indicative of one dimensional diffusion process at the direction normal to the grating stripes. In this way, anisotropic diffusion can be measured simply by changing the direction of the substrate with respect to the grating symmetry. Second Harmonic Generation (SHG) diffraction from one monolayer (1ML) of CO on Ni(111), (Zhu et al. 1988, 1989) and on Ni(110), (Xiao et al. 1991). Coverage dependent diffusion coefficient models were found necessary to understand the experimental data (see e.g. Rosenzwig et al, 1993, Verhoef and Asscher, 1997, Danziger et al. 2004). An alternative way, utilizing optical linear diffraction method combined with polarization modulation techniques (Zhu et al. 1991, Xiao et al, 1992, Wong et al. 1995, Fei and Zhu, 2006) has yielded a more sensitive and accurate calculation of the anisotropic diffusion coefficient of CO on Ni(110), (Xiao et al, 1993).

Selective patterning of H on top of Si(111) surface (Williams et al. 1997) was demonstrated via pre-patterning a thin layer of Xe adsorbed on the Si surface that has reduced the sticking coefficient of H on Si by more than an order of magnitude. This way the authors were able to pattern chemisorbed H while avoiding high power laser pulses impinging on the surface thus preventing possible laser induced surface damage.

We have recently introduced a procedure that adopts the concept of laser-induced ejection of a weakly bound, volatile layer, applied for generation of size-controlled arrays of metallic clusters and sub-micron wide metallic wires. This buffer layer assisted laser patterning (BLALP) procedure utilizes a weakly bound layer of frozen inert gas atoms (e.g., Xe) or volatile molecules (e.g., CO₂ and H₂O) that are subsequently exposed to metal atoms evaporated from a hot source. It results in the condensation of a thin metal layer (high evaporation flux) or small clusters (low flux) on the top surface of the buffer layer. The multi-layered system is then irradiated by a short single laser pulse (nsec duration) splits and recombines on the surface in order to form the interference pattern. It results in selective ablation of stripes of the volatile buffer layer along with the metallic adlayer deposited on it. This step is followed by a slow thermal annealing to evaporate the remaining atoms of the buffer layer with simultaneous soft landing of metallic stripes on the substrate. In other words, this procedure combines the method for generating grating-like surface patterns by laser interference (Zhu et al. 1988, Williams et al. 1997) with a buffer-assisted scheme for the growth of metallic clusters (Weaver and Wadding, 1991, Antonov et al., 2004).

Employing a single, low power laser pulse, the BLALP technique has been utilized to form parallel stripes of potassium (Kerner and Asscher, 2004a, Kerner et al., 2006), as well as continuous gold wires (Kerner and Asscher, 2004b) strongly bound to a ruthenium single crystal substrate.

An extensive study of surface diffusion of gold nanoclusters on top of Ru(100) and p(1x2)-O/Ru(100) was preformed utilizing the BLALP technique (Kerner et al., 2005). The authors discuss the smearing out of gold clusters density grating deposited on the substrate due to one dimensional diffusion process. Figure 1 describes the smearing out of a density grating created after evaporating 1nm of gold onto 60ML of Xe adsorbed on Ru(100) surface.
Heating a similar grating structure in air to 600K for 2h has resulted in no noticeable effect on the metal clusters forming the grating. It is believed that heavy oxidation of the Ru substrate under these conditions acts as an anchor and inhibited the cluster diffusion. Smearing out of the density grating had little or no effect on the size distribution of the gold clusters, suggesting no significant sintering and coalescence of the clusters under these conditions.

Fig. 1. AFM images of a high density gold cluster coverage grating created via BLALP scheme, evaporating 1nm of gold on top of 60ML of Xe. All images were taken at ambient environment. A) After annealing in vacuum to 300K and kept at room temperature. B) After annealing to 450K at 3K/s and quenched back to room temperature. Images are courtesy of Kerner et al., 2005.

Monitoring clusters' diffusion in-situ is possible by simultaneously recording the first order linear diffraction signal decay resulting from shining low power (5mW) He-Ne cw laser on such grating while heating the substrate. The 1st order diffraction decay can be correlated to the diffusion coefficient of the clusters on the substrate (Zhu et al., 1991, Zhu, 1992). Due to the large temperature range in which diffusion takes place in this system (~250K), performing isothermal measurements is impractical. Introducing a novel, non-isothermal diffusion method has enabled Kerner et al. to circumvent the complexity of isothermal diffusion measurements in this system and has provided the authors a method to measure the diffusion of a range of cluster sizes and density distributions on top of Ru(100) and on top of p(1x2)-O/Ru(100). On both surfaces, it was found that the diffusion coefficient is density (coverage) independent. The activation energy for diffusion was sensitive to the cluster size on the bare Ru(100) surface but only weakly dependent on cluster size on the p(1x2)-O/Ru(100) surface. This arises from the weak interaction of the gold clusters with the oxidized surface and in particular the incommensurability of the clusters with the underlying oxidized substrate.
1.2 Pulsed laser driven lithography and patterning

Direct laser interference lithography/patterning involving selective removal of material from the surface of a solid sample employing two or more interfering laser beams has been used in a large variety of applications. These techniques were utilized for polymers patterning, micromachining, semiconductor processing, oxide structure formation and for nano-materials control over magnetic properties (Kelly et al., 1998, Ihlemqnn & Rubahn, 2000, Shishido et al., 2001, Chakraborty et al., 2007, Lasagni et al., 2007, 2008, Leiderer et al., 2009, Plech et al., 2009).

A modified version of the BLALP technique that involves laser patterning of the clean volatile buffer layer prior to the deposition of the metal layer has also been introduced to generate smooth metallic stripes on metallic (Kerner et al., 2004c, 2006) as well as oxide (SiO$_2$/Si(100)) substrates. The unique advantage of BLALP is the low laser power needed for patterning, which prevents any damage to the substrate.

The importance of laser-driven ejection of a layer of weakly bound material from light absorbing substrates has motivated a number of experimental (Kudryashov & Allen 2003, 2006, Lang & Leiderer, 2006, Frank et al., 2010) and computational studies (Dou et al., 2001a, 2001b, Dou et al., 2003, Smith et al., 2003, Gu & Urbassek, 2005, 2007, Samokhin, 2006) targeted at revealing the fundamental mechanisms responsible for the layer ejection. The physical picture emerging from these investigations suggests that fast vaporization (explosive boiling) and expansion of the superheated part of the layer adjacent to the hot substrate provides the driving force for the ejection of the remaining part of the layer.

In this paper, we report the results of utilizing a single pulse laser patterning, all-in vacuum procedure that can produce practically any sub-micron resolution pattern using an optical system consisting of a masked imaging system.

2. Experimental

The experimental setup has been described elsewhere in detail (Kerner et al., 2005a, 2005b). Briefly, a standard UHV chamber at a base pressure of 5x10$^{-10}$ mbar, equipped with Ne$^+$ sputter gun for sample cleaning and a quadrupole mass spectrometer (QMS, VG SX-200) for exposure and coverage determination and calibration, are used in the experiments. In addition, separate Au, Ag and Ti deposition sources are used, with in-situ quartz microbalance detector for flux calibration measurements. A native oxide SiO$_2$/Si(100) sample is attached via copper rods to a closed cycle helium cryostat (APD) that cools the sample down to 25 K with heating capability up to 800 K (Stein & Asscher, 2006). 700eV Ne$^+$ ion sputtering for sample cleaning was carried out prior to each patterning experiment.

In order to perform laser assisted ablation and patterning measurements, a p-polarized Nd:YAG pulsed laser working at the second harmonic wavelength was used (Sureligh, Continuum λ = 532 nm, 5 ns pulse duration). The laser power absorbed by the silicon substrate was kept lower than 80 MW/cm$^2$ (160mJ/pulse) to avoid surface damage (Koehler et al., 1988). During the experiments we assumed complete thermalization between the SiO$_2$/Si layers with no influence of the thin oxide layer (~2.5 nm thick) on the heat flow towards the adsorbates. Details of Xe template formation via laser induced thermal desorption (LITD) and its characterization are given elsewhere (Kerner & Asscher 2004a, 2004b, Kerner et al., 2005, 2006). After patterning the physisorbed Xe, 12±1 nm thick film
of metal, typically Au or Ag, is deposited on the entire sample. Subsequently, a second uniform laser pulse strikes the surface, ablating the stripes of Xe buffer layer remaining on the substrate together with the deposited metal film/clusters on top and leaving behind the strongly bound metal stripes that are in direct contact with the SiO$_2$ surface. A 2±1 nm thick layer of Ti deposited over the SiO$_2$ surface prior to the buffer layer adsorption and metal grating formation, ensures good adhesion of the noble metals to the silicon oxide substrate and avoid de-wetting (Bauer et al., 1980, George et al., 1990, Camacho-López et al., 2008). The Ti adhesion layer does not affect the optical properties of the substrate (Bentini et al., 1981).

Patterning through a mask is introduced here for the first time, utilizing a single uniform laser pulse. The mask is a stainless steel foil 13µm thick that contains the laser engraved word "HUJI" (Hebrew University Jerusalem Israel). An imaging lens was used in order to transfer the object engraved on the mask onto the sample plane while reducing its size according to the lens formula:

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$$  \hspace{1cm} (2)

$u$: mask-lens distance (120 cm).
$v$: lens-sample distance (24 cm).
$f$: focal length of the lens (20 cm).

Ex-situ characterization of the resulting patterns was performed by HR-SEM (Sirion, FEI), AFM in tapping mode (Nanoscope Dimension 3100, Veeco) and an optical microscope (Olympus BX5).

3. Results and discussion

3.1 Metallic line patterning via laser interference

Metallic lines were patterned directly on the SiO$_2$/Si sample using Lift-off (Kerner et al., 2004c, 2006) and BLALP schemes. Using CO$_2$ as the buffer material it was possible to perform a BLALP patterning process under less stringent cooling requirements than those previously used with Xe as the buffer material (Rasmussen et al. 1992, Funk et al., 2006). Figure 2 demonstrates the results of patterning 12 nm thick layer of Au using 10ML of CO$_2$ as the buffer material.

Although metal stripes obtained this way demonstrate good continuity, their texture is corrugated since these stripes are composed of metal clusters soft-landed on the substrate after annealing the sample to room temperature, according to buffer layer assisted growth (BLAG) procedure (Weaver & Waddill 1991). Using this scheme, metal clusters are evenly distributed in the areas between the metal stripes. Molecular dynamics (MD) simulations describing the laser ablation of the buffer material from a silicon surface have indicated that under the experimental conditions adopted in the current study, evaporative buffer material removal scheme is dominant (Stein et al., 2011). This evaporative mode of ablation, unlike the abrupt or explosive ablation that dominates at higher laser power, does not necessarily removes all the metal layer or clusters that reside on top. In this case, therefore it is likely that some of the metal evaporated on top of the buffer could not be removed by the laser pulse, and was finally deposited on the surface as clusters.
Fig. 2. AFM image of BLALP patterning of 12 nm thick layer of Au deposited on top of 10ML CO$_2$ buffer material on a SiO$_2$/Si(100) sample at 25 K. Laser power was 14 MW/cm$^2$.

Figure 3 illustrates the two different Xe removal mechanisms. Figures 3A and 3B demonstrate intense evaporation and explosive desorption of Xe from Si(100) surface, respectively (Stein et al., 2011).

Figure 4 demonstrates lift-off patterning: after patterning 80ML of Xe using laser power of 12MW/cm$^2$, 18 nm of Au were deposited on the sample. A second, uniform pulse at a power of 9MW/cm$^2$ was subsequently applied in order to remove the remaining Xe and metal on top.

The fragmented and discontinuous nature of the metal stripes resulting from this patterning procedure on SiO$_2$/Si samples is apparent. This shape is due to the poor adhesion (and de-wetting) of Au on SiO$_2$ (Bentini et al., 1981, George et al., 1990, Lani et al., 2006). Overcoming this problem requires evaporation of 2±1 nm Ti on top of the entire SiO$_2$ surface as an adhesion and wetting layer (Bentini et al., 1981). Figure 5 displays the effect of Ti evaporation on the integrity and smoothness of the metal stripes patterned via the lift off procedure.

The images in figure 5 reveal a clear power effect which is a characteristic feature of the lift-off patterning scheme. Raising the laser power leads to widening of the ablated buffer troughs as the sinusoidal temperature profile increases. Into these wider troughs metal is
evaporated, eventually (after the second pulse) forming smooth and continuous wires, ideally across the entire laser beam size. Increasing the pulse power by 40% has led to wider stripes from 700 nm to 1300 nm, see Fig. 5A and 5B.

Fig. 3. Snapshots from MD simulations performed on 7744 Xe atoms adsorbed on top of Si(100) surface. A and B represent evaporative and explosive desorption while irradiating the surface by 12 and 16MW/cm$^2$ pulse power, respectively. Snapshots were taken at 9.4 ns (A) and 6.6 ns (B) from the onset of the laser pulse.

Electrical resistance measurements were performed on these metallic wires. On a patterned sample a set of 100X100µm metallic pods with ohmic contact to the patterned wires were prepared by e-beam lithography in order to ex-situ measure the resistivity of the silver metal wires. The resistivity measurements were calibrated against a similar measurement performed using Au wires of identical dimensions, produced via e-beam lithography. Measurements have revealed that the resistivity of the laser patterned wires were about 40% (on average, calculated from four different measurements performed at different locations on the sample) higher compared to the e-beam prepared Au, 197 and 140Ω for the laser-patterned Ag and the e-beam Au over a line distance of 24.2µm, respectively. Annealing the patterned sample at 600K for two hours in ambient conditions has led to higher resistivity by 60%, as a result of oxidation and aggregation of the Ag wires, increasing from 197 to 318Ω. In contrast, the annealed Au wires have shown a 75% drop in resistivity, from 140 to 79Ω, as expected since no oxidation takes place in the case of gold. Figure 6 demonstrates the aggregation occurs within the Ag stripes to form spherical clusters caused by annealing the sample to 600K for two hours in ambient conditions.
Fig. 4. SEM image of lift-off patterning of 18 nm Au on top of SiO$_2$/Si surface. The power of the first and second laser pulses was 12 and 9 MW/cm$^2$, respectively. Inset depicts the corrugated (and fragmented) texture of the resulting metal wires.

Fig. 5. AFM images of lift-off patterning procedure including line scan along the red line. A) 15 nm of Ag on top of a coverage grating formed via a 50 ML Xe on Ti/SiO$_2$/Si surface. First and second pulse power were both of 10 MW/cm$^2$. B) 12 nm of Ag on top of grating produced with 70 ML Xe on top of Ti/SiO$_2$/Si surface. Both the first and second pulses were at 14 MW/cm$^2$. 

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Fig. 6. Annealing effect on a lift-off patterned sample consisting of 20 nm of Ag evaporated on 70ML of Xe grating on Ti/SiO$_2$/Si surface. A and B: AFM images in ambient conditions before and after annealing to 600K, respectively.

3.2 Laser patterned mask imaging

General application of the buffer layer assisted laser patterning scheme requires the ability to perform any desired shape and structure. This can be achieved by striking the buffer covered substrate with a laser beam that has been partially blocked by a patterned mask. In order to demonstrate the ability to pattern via a mask, a stainless steel foil, 12.7µm thick that contains the laser engraved word "HUJI" as our mask, the size of the word-object was 4X1.3mm. After passing through the mask, the laser pulse traveled through a lens in order to reduce-image the HUJI word on the sample's plane. Five times reduction required a 20 cm focal length lens at a distance of 120 and 24 cm from the mask and sample, respectively. Using this imaging lens required a dramatic reduction of laser power in order to avoid surface damage. Figure 7 demonstrates the lift-off lithography of the word "HUJI" on top of Ti/SiO$_2$/Si surface.

A 60 ML Xe deposited on Ti/SiO$_2$/Si(100) sample was prepared to demonstrate the mask-laser patterning. A single pulse, 0.8 MW/cm$^2$ (2.5 mJ/pulse) penetrating through the mask and the lens system was employed as described above. Prior to the second, uniform laser pulse striking the entire sample without the mask and the lens, 12±2 nm Au was evaporated on top of the HUJI patterned Xe buffer layer covered substrate. The sample was subsequently heated to room temperature and removed from the vacuum chamber for characterization using AFM and optical microscopy.

Employing a weaker first laser pulse at a power of 0.5 MW/cm$^2$ (1.5 mJ/pulse) prior to the evaporation of gold, has resulted in a narrower line width of the final pattern although with somewhat poorer quality (not shown), as was previously demonstrated in the case of two interfering beams forming parallel metallic stripes (see Fig. 5 above). This behavior, of
Fig. 7. A) Optical microscope image of the word "HUJI" following lift-off lithography written by 12±2 nm thick Au on Ti/SiO$_2$/Si surface. First pulse 0.8 MW/cm$^2$, Xe buffer thickness was 60ML. B) AFM image demonstrating the edge of the patterned letter "H". C) A height profile taken along the line in image B.

narrowing the line width of a given feature while lowering the pulse power is a result of the laser pulse Gaussian spatial profile. As the first pulse power goes up, a wider part of the pulse reaches ablation threshold of the buffer material (Xe in this case), allowing more buffer material to be removed from the surface. Line narrowing through pulse power lowering is one of the characteristics of the lift-off patterning scheme. This power knob is a unique, very practical and easy to use for various applications, allowing patterning far from substrate laser induced damage threshold. One should bear in mind that the total pattern quality is highly dependent on the first pulse power uniformity as random variations in the laser pulse profile will be manifested in overall lower quality pattern, especially while employing near ablation threshold power.

By tuning the first pulse power up from 0.5 MW/cm$^2$ (1.5 mJ/pulse) to 0.8 MW/cm$^2$ (Fig. 7A) we were able to significantly improve the image quality while introducing a minor increase in the size of the object, all without changing the optical imaging parameters.
Image 7B represents a characteristic edge image of the patterned object, utilizing a tapping mode AFM. One can clearly notice the corrugated texture of the evaporated gold film on top of the Ti/SiO$_2$/Si surface, featuring the 3D growth of multilayer Au on top of metal surfaces. Looking at the line profile presented in fig. 7C, the sharp drop representing the edge of the letter "H", as shown in the image. The sharp drop from the top of the gold film to the bottom of the Ti surface occurs in a lateral distance of $\sim$50 nm, ten times smaller than the 532 nm wavelength used in this experiment, evidence to the abrupt, temperature exponential dependent ablation of the Xe buffer. Even in our simple, basic optical design consisting of a mask and lens, we were able to arrive at the sharply resolved lines shown in Fig. 7A. Simple reduction in the ablating laser wavelength and by meticulously measure the relevant distances (objective- lens, lens- surface) one can further enhance this process' resolution.

This simple, all-in-vacuum fast and clean patterning procedure does require highly accurate and robust, through vacuum imaging technique in order to avoid standard diffraction based distortions of the desired features to be patterned.

4. Conclusions

The role of weakly bound atomic and molecular buffer layers in forming periodic coverage density has been discussed as a versatile tool to study in-vacuum metallic nano-particles growth and their surface diffusivity, an important aspect of catalysis. In addition, we have demonstrated the application of the buffer layer method to pattern a Ti/SiO$_2$/Si surface using pulsed laser lithography through a simple optical system consisting of a mask and an imaging lens. Feature (the letters HUJI) size reduction of 1:5 has been demonstrated with AFM imaged sharp edges that are three orders of magnitude narrower than a letter size. Focusing on weakly bound buffer materials for the patterning method has enabled us to use low power laser, significantly below surface damage threshold. Employing the buffer assisted laser patterning method there is virtually no limit to the pattern that can be transferred to practically any (light absorbing) substrate.

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6. References


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The book starts with basic overview of physical phenomena on laser-matter interaction. Then it is followed by presentation of a number of laser applications in the nano-particles and thin films production, materials examination for industry, biological applications (in-vitro fertilization, tissue ablation) and long-range detection issues by LIDARs.

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