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A Simple Technique for Submicron Scale Patterning of Silver Using Visible Light Interference

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A novel, one step and simple methodology for the fabrication of submicron scale silver patterns is demonstrated. The photosensitivity of an organic silver salt has been utilized for this purpose of fabrication. The silver-organometallic compound is converted to metallic silver selectively in the illuminated regions. Surface morphology was studied by scanning electron microscopy (SEM). Energy dispersion spectroscopy (EDS) shows the presence of silver in the developed film. X-ray photoelectron spectroscopy (XPS) confirms the formation of metallic silver. Feature sizes of the order of 200 nm have been achieved using this technique.

Keywords: Organometallic, photolysis, silver micro patterning

1. Introduction

The ability to generate submicron and nanometer scale metal patterns has a variety of applications in both microelectronics and large area electronics (1). The technology currently used in the production of high resolution metal patterns involves several steps. Optical lithography involves creating patterns through projecting ultraviolet (UV) wavelength radiation using a mask (2). The mask based photolithography adopted by industries is the current standard for micro fabrication. This method requires deposition of metal followed by a layer of resist. The resist is patterned and then metal is selectively etched to get the desired pattern. Although this is a well established technique it has many disadvantages. This technique requires complex and expensive instrumentation including a high vacuum system. Apart from photolithography, scanning probe microscopy (SPM) lithography, E-beam lithography, micro contact printing, ink-jet printing etc have also been used for pattern generation (3, 4). The direct deposition of metals by photodecomposition of organometallic complexes is particularly suitable for periodic pattern generation and has attracted the attention of many researchers in recent years (5, 6). To the best of our knowledge, most of the researchers have used a mask for the selective decomposition of metal precursors.

Here we report a simple technique to fabricate silver patterns using photosensitive silver organometallic compounds without using any physical mask. In this process we have used the interference of laser beams for the fabrication of metal patterns (7). This technique is versatile and could potentially be used for any photo sensitive organometallic compounds. Ease of processing and the reduction in number of steps can significantly lower the cost of fabrication.

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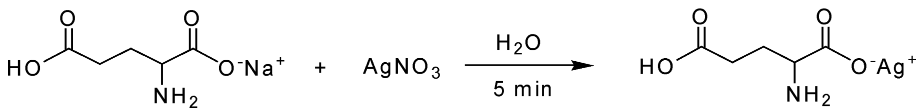
2. Experimental

2.1. *Materials used and preparation of organo silver precursor*

Monosodium L-glutamate and silver nitrate were purchased from Sigma-Aldrich. Silver glutamate was prepared by the procedure reported by Tabie et al. (8). Sodium salt of glutamic acid was mixed with silver nitrate solution in the dark to give silver glutamate. Silver glutamate was dissolved in ammonia ethanol solution (30 ml, ammonia water: ethanol: water-1:6:3) and used for the study.

25 ml of 0.02 M monosodium L-glutamate solution was mixed with 25 ml of 0.02 M silver nitrate solution and stirred for 5 min at room temperature. The precipitate was filtered in the dark and air-dried at room temperature. Then the silver glutamate (1.5 g) was dissolved in ammonia ethanol solution and stored in refrigerator.



2.2. *Film deposition and patterning*

The thin film of silver precursor was obtained by spin coating on a glass substrate. We have tried different spin speeds, and the samples used for these studies were coated at 700 RPM on a glass substrate. For the pattern generation, the sample was illuminated with a continuous coherent beam from an Ar^+ ion laser at 514.5 nm. Figure 1 shows the experimental setup used in this work.

The incident beam intensity was 100 mW/cm^2 and the angle (θ shown in Fig. 1) was 14 degrees, leading to pattern periodicity of 1 micron. The interference fringe contains alternate bright and dark regions. The presence of light initiates the decomposition of organometallic silver precursor leading to the formation of metallic silver. The total time of exposure was 30 min and the observed diffraction efficiency was 2%. Subsequently, in the development process, the unexposed regions were washed off using the solvent. Through the above process, the direct deposition of silver metal is achieved using the photosensitive compound. This process significantly reduces the number of steps involved and can easily be extended to large area patterning.

2.3. *Characterization*

The morphology of the patterned film was studied by SEM (JEOL FESEM). UV-Visible absorption spectra were recorded using a UV/Visible Lambda 9 spectrometer employing a double-beam direct ratio recording system. For background correction, a clean blank glass slide was used. EDS studies were done using EDAX coupled with FESEM which provides elemental composition at the selected regions. XPS (in VG ESCALAB MKII instrument) has been used to confirm the formation of metallic silver.

3. Results and discussion

3.1. *UV-Vis absorption of the silver precursor*

Figure 2 shows the UV-Vis absorption of a silver glutamate thin film on a glass substrate. It is clear that the silver precursor has very small absorption at 514.5 nm, which has been used for the pattern generation. Due to the small absorption, fabrication of silver lines of around 200 nm was achievable, although the expected line width was about 500 nm. On the other hand, the small absorption necessitates a long exposure time for pattern generation.

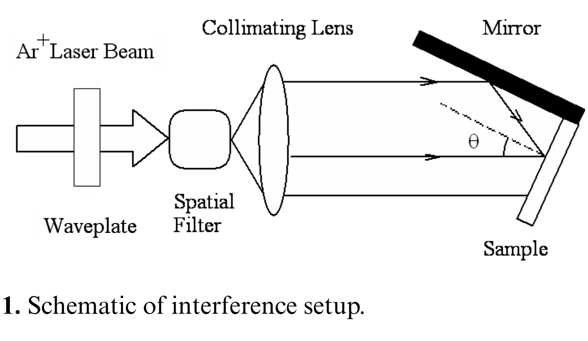


Fig. 1. Schematic of interference setup.

3.2. *Morphology of the silver lines*

The morphology of the generated pattern has been studied by SEM. Figure 3 shows the SEM image of the pattern having a line width of 200 nm with a periodicity of 1 micron. An SEM image obtained at higher magnification is provided in Figure 4. This image shows that silver particles are well connected and form a continuous line at the scale of few tens of nanometers. However, the adhesion of the silver particles to the substrate is poor, on washing with developer the lines tend to get crooked. SEM also confirms that there is not much silver in the gaps after developing the patterns.

3.3. *EDS spectra of generated pattern*

This technique utilizes the X-rays that are emitted from the sample upon bombardment of the electron beam. This provides the elemental composition of the sample. The energy of the X-ray is the characteristic of the element from which the X-ray is emitted. Figure 5 shows the EDS spectra of the line in the SEM image. It clearly shows that the lines contain silver. The other elements present are from the glass which has been used as substrate.

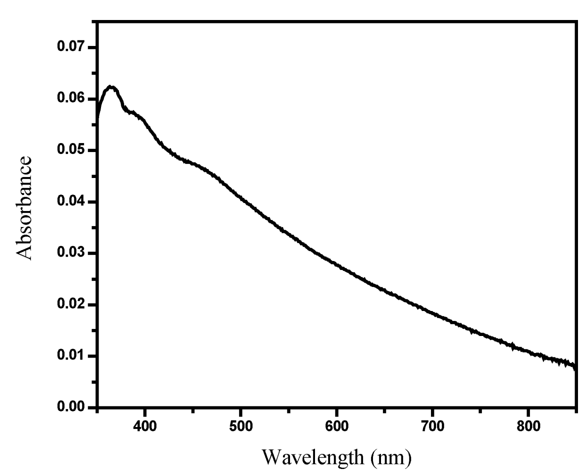


Fig. 2. UV-Vis absorption spectra of the thin film of silver glutamate.

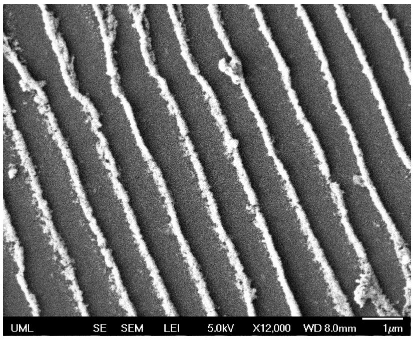


Fig. 3. SEM image of the patterned silver after washing off the unexposed precursor.

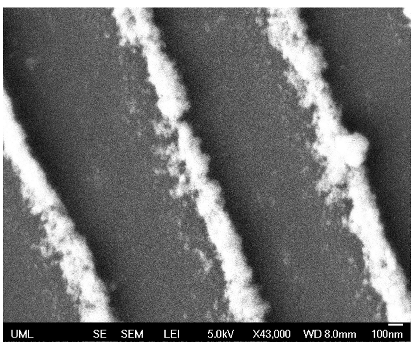


Fig. 4. SEM image of the patterned silver lines at higher magnification.

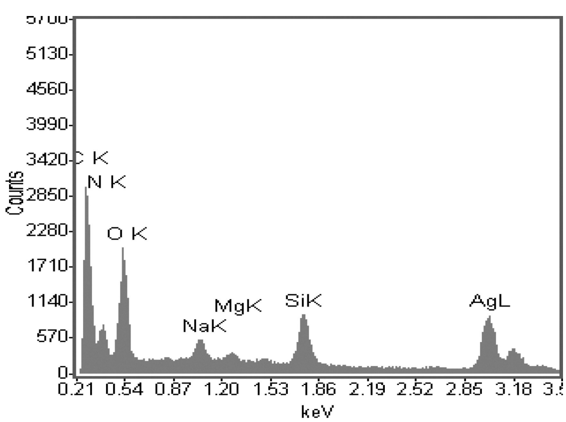


Fig. 5. EDS spectra of the patterned silver lines.

3.4. *XPS results*

XPS was performed with a base pressure of less than 1×10^{-9} Torr using Mg Kα X-rays source ($h\upsilon = 1253.6$ eV). The photoelectrons were detected with a concentric hemispherical analyzer in constant pass energy mode using pass energy of 20 eV at a takeoff angle (the angle between the normal to the entrance of the analyzer and the plane of the sample) of 90°. The decomposed silver organometallic was also analyzed by XPS. This analysis shows Ag 3d

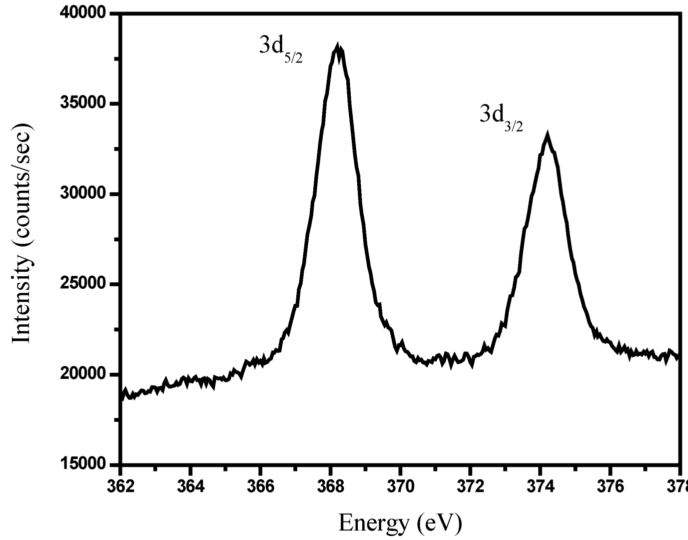


Fig. 6. Ag 3d XPS spectra of the decomposed silver organometallic.

peaks at 368 eV and 373 eV (Fig. 6). These peaks coincide with appropriate binding energies for silver metal and correspond to the $3d_{3/2}$ and $3d_{5/2}$ core levels, respectively (9). The XPS result confirms the formation of the metallic silver as a consequence of the light induced degradation of silver organometallic.

4. Conclusions

A simple and easy technique has been demonstrated for the generation of submicron periodic metal patterns. This method is versatile and does not require photo resist and mask for the patterning process. The EDS and XPS studies confirm the formation of metallic silver by photo decomposition of silver salt. The line width obtained here is around 200 nm with periodicity of 1 micron. The interference technique reported here is expected to be cost effective for fabrication of periodic metallic patterns as it is substantially simpler than other existing techniques.

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