1-25-2011

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Keywords

Ames Laboratory, Physics and Astronomy

Disciplines

Materials Science and Engineering | Optics | Semiconductor and Optical Materials

Comments

This article is from *Journal of Micro/Nanolithography, MEMS, and MOEMS* 10 (2011): 013011, doi:10.1117/1.3541794. Posted with permission.

J. Micro/Nanolith. MEMS MOEMS 10(1), 013011 (Jan–Mar 2011)

Fabrication of submicron metallic grids with interference and phase-mask holography

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Abstract. Complex, submicron Cu metallic mesh nanostructures are made by electrochemical deposition using polymer templates made from photoresist. The polymer templates are fabricated with photoresist using two-beam interference holography and phase mask holography with three diffracted beams. Freestanding metallic mesh structures are made in two separate electrodepositions with perpendicular photoresist grating templates. Cu mesh square nanostructures having large (52.6%) open areas are also made by single electrodeposition with a photoresist template made with a phase mask. These structures have potential as electrodes in photonic devices. [DOI: 10.1117/1.3541794]

Subject terms: holographic interferometry; photonic bandgap materials; complex nanostructures; fabrication and characterization nanoscale materials; methods of micro- and nanofabrication.

Paper 10115R received Oct. 13, 2010; revised manuscript received Dec. 6, 2010; accepted for publication Dec. 17, 2010; published online Jan. 25, 2011.

1 Introduction

Metals are often used in electronic devices for their high electrical and thermal conductivity, but high absorption prevents their use as transparent optical materials except for the case of very thin films. However, metallic gratings and meshes are good candidates for transparent electrodes. Energy-efficient devices for both solar collection and light emission demand economical and durable transparent electrodes. Metal oxides (indium and zinc-based oxides) have been used as transparent electrodes due to low absorption in the devices' spectral ranges. However, thin metal oxides suffer from lifetime degradation due to oxygen migration. Alternatively, transparent metallic electrodes have been considered as potential replacements for such oxide electrodes[1,2] despite the fact that metals are optically opaque unless they are thinner than optical skin depth or have a significant volume of voids. Optical studies of metal films having periodic holes or slits have shown high optical transmission and good electrical conductivity.[3,4] The transmission can even exceed the ratio of open area to the entire sample area at certain wavelengths. This can be explained by surface plasmon resonance—collective oscillation of electrons on the metal-insulator interface. In addition to the high conductivity of metals, transparent metallic structures are robust and flexible so they are suitable for many optical and optoelectronic devices.

There have been many attempts to make highly transmitting metallic structures. These include fabricating periodic holes in a metal thin film by e-beam lithography or focused ion milling but are limited in feasibility for large areas. Although photolithography has been widely used in industry and is a well-established technique, high-resolution photolithography requires expensive facilities. One alternative is two-beam laser holography, which can make grating structures as small as half of the wavelength of the laser without clean-room facilities.[5] There are two simple ways to make metallic wires using polymer patterns. One is by selectively etching deposited metals using a patterned polymer as a mask.[6] In this case, the width of the etched metal

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structures after etching is approximately the same as that of the pattern or slightly less due to undercutting. Etching with the pattern can yield a smooth top surface as deposited but usually gives rough sidewalls due to irregular etching rates. Another method involves filling the empty channels in the polymer pattern with metal via electrodeposition.[7] The metal filled in the channels has the inverse structure as that of the template and has sidewalls nominally as smooth as the template. In this case, however, the top surface may not be as flat due to variation in growth rates caused by a nonuniform electric-field distribution during the metal growth.

Holographic interference lithography (HIL) has been widely used in making periodic structures such as gratings,[8] cylindrical pillars,[9] and even complex photonic crystal structures.[10–13] Interference holography uses an interference pattern rather than a photomask. New methods of making narrow metallic mesh structures having more open area using diffractive phase masks have been developed.[14,15] The typical feature shape of a double exposure in interference holography is a cylinder that is circular in the top view.[8,9] However, in this paper we present that two-dimensional (2-D) square metallic mesh structures can be made with two successive fillings in empty channels of the gratings. This process requires an electrodeposition in the channels of the photoresist grating and a second electrodeposition in the channels of the gratings patterned crossed by 90 deg on the first electrodeposited one. Furthermore, we also present that photolithography using diffracted beams of a phase mask and subsequent single electrodeposition also makes metallic mesh structures with a large fraction of open area.

2 Experimental details

Laser interference holography with a Lloyd's mirror setup has been used for large-area uniform grating structures with a simple optical setup as in Fig. 1(a).[16] The setup consists of a UV microscope objective, spatial filter, and rotational stage with mirror. A linearly polarized light of 364-nm wavelength of a single-mode Ar-ion laser was used for a coherent light source. A spatial filter having a 10 μm diam was placed at the focusing point of the 10X UV lens to eliminate distortions from optical components and scattering from dust. An adhesion promoter, MCC primer (Microchem Inc., Newton, MA, USA), was spin-coated and baked at 120°C for 2 min before spin-coating the photoresist, AZ HiR 1075 (AZ Electronics, Branchburg, NJ, USA), at 4000 rpm. The spin-coated photoresist was baked in the oven at 60°C for 30 min to evaporate the solvent. The sample was mounted on rotating stage with an Al mirror mounted perpendicular to the sample surface. A typical dose is ~200 mJ for mask pattern fabrication. A postexposure bake was done at 90°C on hot plate for 90 s to fully cross-link the polymer. The sample was developed for 60 s by gentle stirring in the developer (AZ 300 MIF). The thickness of photoresist including the adhesion promoter is 750 nm measured from a cross-sectional image with a JEOL 840 scanning electron microscope (SEM).

To make metallic structures having circular or square holes, the photoresist pattern was made on indium tin oxide (ITO)–coated glass to facilitate electrodeposition of metals. Alternatively, a few nanometers-thick metal-coated glass can be used as a substrate instead of ITO-coated glass. Cu was electrochemically deposited by applying 50-Hz pulse reversed 10 mA ac current. Forward +5 V for 10 ms and reverse –3 V for 5 ms were applied to constitute one period. Pulse reverse plating helps initial nucleation of Cu and enhances uniform film growth. The electrodeposition was stopped before overfilling the channels. Then, the photoresist was removed by immersion in Remover PG (Microchem Inc.) for 30 min. The thickness of metals can be controlled by electrodeposition current and time.

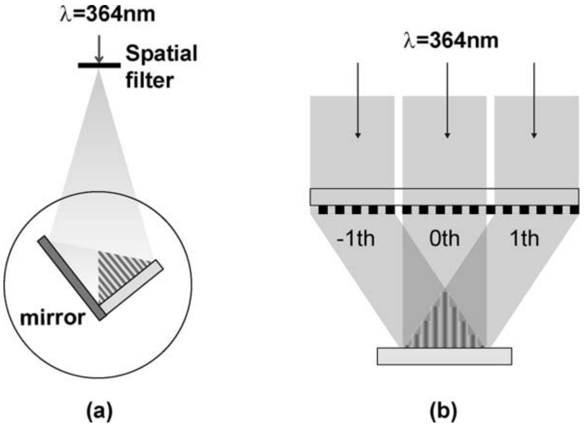

Fig. 1 Experimental diagram for (a) two-beam interference holography and (b) three-beam interference holography with diffractive phase mask.

Furthermore, we can make metallic mesh structures having large open-area square holes with one electrodeposition using a phase mask. The phase mask was made with photoresist on a glass using two-beam interference holography. The pitch of the phase-mask grating was chosen to have only zero- and first-order diffraction. The pitch of phase-mask grating must be smaller than twice the laser wavelength, 364 nm, of the Ar-ion laser to avoid second-order diffraction. For a phase mask having second-order diffractions, the photoresist can be placed away from the phase mask so the second-order beam diffracted does not reach the photoresist. The pitch of the phase-mask grating was 750 nm, and the mask was placed 1 cm away from the sample to avoid second-order diffraction. To fabricate a large sample, the phase differences between the three interfering beams are kept constant by ensuring that the sample is placed parallel to the phase mask. The Cu structures made with the phase mask are narrower than those made with conventional two-beam holography and are close to square in cross section.

3 Results and Discussion

It is easy to make grating structures over a large area with a simple Lloyd's mirror optical setup. The grating pitch (or period) Λ, described as Eq. (1), can be easily changed by adjusting the incidence angle (θ) or wavelength (λ) of the light source,

$$\Lambda = \frac{\lambda}{2\sin\theta} \tag{1}$$

Even though interference holography has benefits in making large-area samples, making an arbitrary shape is difficult. Typically, the width of individual grating lines is about half of the period. The duty cycle (grating width/period) can be tailored by controlling the dose either by changing exposed

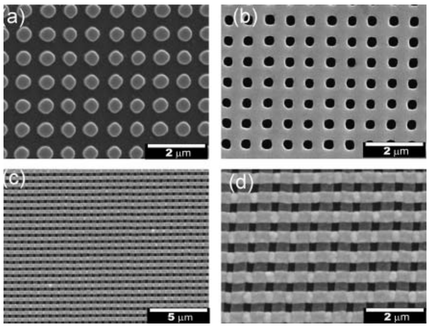

Fig. 2 SEM images of (a) 2-D cylindrical photoresist pattern made by double exposure with two-beam holographic interference and (b) its Cu mesh structure after electrodeposition and photoresist removal. (c) Cu mesh structures made by two electrodepositions filling the empty channels of two perpendicular grating patterns. The second-layer photoresist was patterned after the first-layer metal layer deposition. (d) High-magnification image of square Cu mesh.

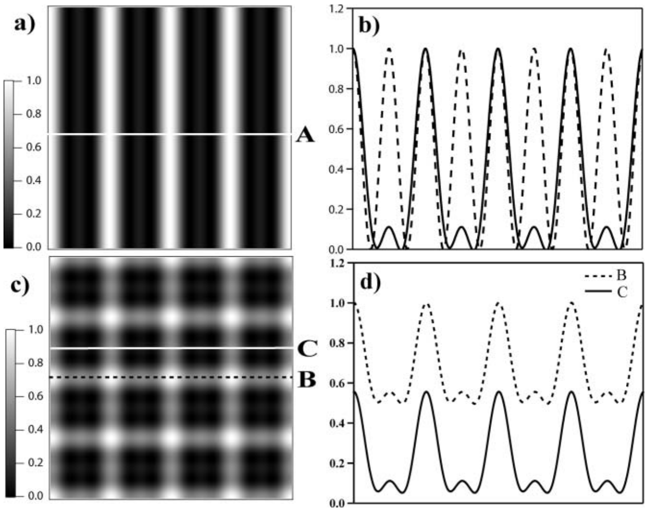

Fig. 3 (a) Simulation of the intensity map of three-beam interference and (b) intensity across the line A (solid line) and that of two-beam interference (dotted line). (c) 2-D intensity map of the double-exposed three-beam interference with 90-deg rotation and (d) intensity along lines B (dotted line) and C (solid line).

time or light intensity. Because the response of the photoresist does not vary linearly with the dose, it is difficult to precisely control the grating width, especially for submicrometer pitch. A duty cycle of 0.4–0.6 can be made by controlling dose intensity, but narrower or wider is difficult to achieve by dose control.[5,14]

For 2-D structures, the photoresist was exposed twice with a 90-deg rotation between exposures. The intensity of double exposure is the superposition of two sinusoidal beams. The positive (or negative) photoresist exposed above (or below) a critical intensity has dissolved during developing and has circular patterns. The photoresist pattern is a 2-D cylinder, as in Fig. 2(a), and the final Cu structure is the inverse structure of the photoresist and has circular holes after polymer removal, as in Fig. 2(b).[17] To fabricate metal structures having square holes, either two separate depositions with straight-line templates or single electrodepositions with templates having a square shape is required. The first method for square-shape patterns was done as follows: The first Cu deposition fills the channels of a photoresist grating made by a single exposure of the two-beam interference. The second layer of photoresist is patterned after rotating by 90 deg on the top of the Cu grating. And the second Cu deposition fills the channels of the photoresist perpendicular to the first layer. After removing photoresist, the remaining Cu mesh has square holes, as in Figs. 2(c) and 2(d), and can be easily detached from ITO glass making freestanding metallic mesh structures. Because each layer has 50% open area, meshes made by two electrodepositions have ∼25% open area. Also the cross area between two Cu layers is thicker than other areas.

To fabricate large open-area metal-mesh structures with a single electrodeposition (the second method for square-shape patterns), a pattern was made from the interference of three diffracted beams after passing through the phase mask. The interference of coherent beams is the sum of each plane wave and described as follows:

$$I = I_0\{3 + 4\cos(kx\sin\theta + \Delta\varphi)\cos[kz(1-\cos\theta)] + 2\cos(2kx\sin\theta)\} \tag{2}$$

where I_0 is the incident laser beam intensity, $\Delta\varphi = \varphi_1 - \varphi_0$ is the phase difference between the first- and zeroth-order beam and θ is the first-order diffraction angle from the normal. Equation (2) has additional phase difference $\Delta\varphi$ compared to Eq. (2) in Ref. 9. The second term is the interference between the first- and zeroth-order diffracted beams, and the last term is between the first-order diffractions. Figure 3 shows the intensity based on Eq. (2) when $z = = 0$ (on the sample surface). When the positive photoresist is exposed, the high intensity area [bright in Fig. 3(a)] will be dissolved by developer, resulting in thick polymer structures. The pitch of the three-beam interference is same as that of the phase mask, whereas it is half when only two first-order beams are used to make interference pattern as Fig. 3(b). If the channels are filled with a metal and polymer templates are removed, then narrow metallic structures can be obtained. More complex structures can be made with double exposure, in this case, with 90-deg rotation. A 2-D intensity map for two-beam interference has periodic circular shapes, but three-beam interference has a more octagonal shape as Fig. 3(c). The photosensitivity of the photoresist and exposure time determine the width of the gratings. Precise control of the width solely through dose control is difficult due to the nonlinear response of the photoresist and the sharp slope of intensity of the interference pattern. A much narrower intensity profile is possible using phase-mask diffracted beams.

The metallic grating structures were made by Cu electrodeposition into the empty spaces in the patterned ITO

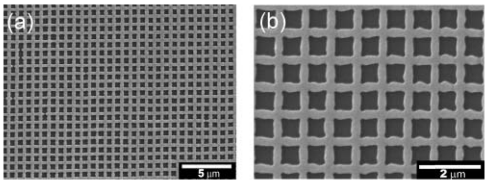

Fig. 4 (a) SEM image of Cu mesh made with phase mask and (b) its high-magnification image after photoresist removal.

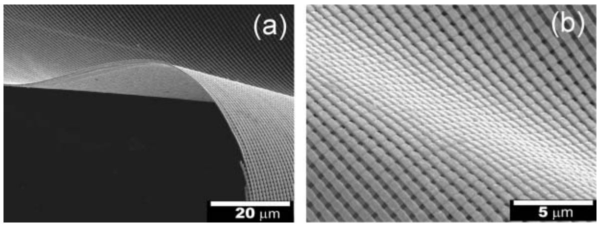

Fig. 5 (a) Freestanding Cu mesh made by two electroplating after each exposure. The mesh was peeled off from the substrate after photoresist removal and (b) its high-magnification image.

substrate as shown in Figs. 4(a) and 4(b). The pitch of the photoresist was set to 750 nm. The Cu mesh structure made with the phase mask has more open area: 52.6% in a unit cell compared to 25–30% for two-beam holography and the shape of the open area is close to rectangular. This large open area in the visible spectrum range can be useful to enhance transmission in a metal electrode. Also, a large area (a few centimeters squared) can be easily made without an e-beam system. To make use of these advantages, the phase difference of the beams must be kept constant for a uniform sample. For uniform intensity across the entire sample area, the sample and phase mask must be parallel. Otherwise, the change of the phase difference between interference beams shifts the intensity line. The optical path-length difference between the two first-order diffracted beams is the same even there is a misalignment in the perpendicular direction to the plane of incidence. The extra phases of two first-order beams due to the misalignment are the same and canceled out in the differences in two-beam interference. When three beams are involved, the extra phase changes due to misalignment between the zeroth- and first-order beams are not canceled in their difference $\Delta\varphi$. A simple calculation shows that they should be parallel within 5.2×10^{-4} deg to make 1-cm^2 uniform area.

The metallic mesh made on the substrate can be easily peeled off for a freestanding form, as in Figs. 5(a) and 5(b). The meshed structure was made by two Cu electroplating in the channels of the photoresist. Cu mesh has ~100-nm thickness and is very flexible. Freestanding mesh should be carefully handed to avoid self folding.

4 Conclusions

In summary, we fabricated Cu metallic mesh structures by electrochemical deposition on photoresist templates made with interference holography and a phase mask. The metallic mesh made by double exposure with interference holography has 2-D circular holes, whereas one made by two sequential electrodepositions with two perpendicular gratings is square in shape but has only a 25% open area. Also, the metal mesh is flexible and peeled off from the substrate to make it freestanding after photoresist template removal. This method is applicable to the mass production of high-quality metallic nanostructures and applications requiring large areas without the need for clean-room or e-beam systems. Alternatively nanoimprint lithography can be used to make polymer templates.[18] Ac pulse reversed deposition enhances the uniform growth of metals. The metallic mesh structures made with a diffractive phase mask are close to square in shape and enable fabrication of structures with larger open areas. The pitch of the phase mask was selected such that only the first-order diffraction appears, and there are only three beams interfering, which results in narrow metallic mesh structures.

Acknowledgments

This work is supported by the Division of Materials Sciences and Engineering, Basic Energy Sciences, U.S. Department of Energy. The Ames Laboratory is operated by Iowa State University for the Office of Science, U.S. Department of Energy under Contract No. DE-AC0207-CH11358. This work also was supported by a Korea Research Foundation grant funded by the Korean Government (MOEHRD) (Grant No. KRF-2008-D00074) and partly supported by a Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MOST) under Project No. F012007-00011760-0.

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Kristen Constant is an associate professor of materials science and engineering at Iowa State University and an associate at Ames Laboratory. She works in Photonic Band Gap Materials and other structures specifically toward designing and fabricating structures that enhance energy efficiency.

Kai-Ming Ho has been a distinguished professor in liberal arts and sciences, Iowa State University, since 1997. He is also a fellow of the American Physical Society, and has outstanding Scientific Accomplishments in Solid State Physics (DOE Materials Science Division) in 1992, and sustained outstanding research in Solid State Physics (DOE Materials Science Division) in 1996. His main research interests are electronic structures of crystal surfaces, molecular dynamic simulations, and propagation of electromagnetic waves in periodic dielectric structures.