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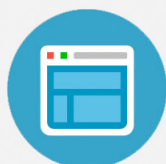
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Fabrication and properties of Cu–Ni mixed-metal periodical array for midinfrared filtering and hydrophobic application

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Cu was grown successfully on Ni film as a conductive layer that demonstrated a stronger Cu (111) preferred crystallographic orientation. Furthermore, we studied the scale effect of various periods of patterned Ni lines separated by variable widths of SiO₂. When Cu was electroplated onto this patterned Ni, it preferentially deposited on the Ni edges adjacent to the SiO₂ stripes, resulting in a Cu–Ni–Cu–SiO₂, Cu–SiO₂–Cu, or Cu–Cu structure, depending on the dimensions of the starting Ni pattern and the deposition time. There are two reflective dips at 2.2 and 8 μm wavelengths using Fourier transform infrared spectroscopy, which revealed a trend of narrower bandwidth in reflective spectra and a redshift effect with increasing deposition time. Interestingly, a hydrophobic surface was also observed due to its particular surface-roughness structures that could be controlled by the deposition time and altered the contact angle from 72° to 110° without coating any extra low free-energy materials. © 2008 American Vacuum Society. [DOI: 10.1116/1.2975202]

I. INTRODUCTION

The controlled fabrication of one-, two-, or three-dimensional periodic structures is important for materials and device engineering. In particular, metal nanostructures are increasingly important building blocks for new materials due to their shape- and lattice-dependent plasmon response and controllable optical and interesting surface properties.^{1–3} Recently, noble metals, including gold, silver, and copper, have increasingly been used to fabricate periodic nanostructures. The periodic metal nanostructures are generally fabricated by nanoimprint,⁴ self-assembly,^{5–9} and many kinds of template techniques, such as anodic alumina membrane,¹⁰ colloidal-crystal nanoparticles,¹¹ and etched-ion track.¹² These periodic nanostructures exhibit superior characteristics on surface plasmonics, excitation, and polarization compared with random nanoparticles or nanoclusters. One metal used in semiconductors, Cu, offers lower resistivity, allows higher current density, and enhances stress and electromigration resistance as compared to Al for applications, such as interconnect structures. Cu is rarely chosen as a periodic-array material because it is difficult to pattern by the dry-etching process and it adheres poorly on the dielectric layer. The above-mentioned fabricating methods can partially overcome dry etching and adhesion problems but they are not easily compatible with semiconductor manufacturing. Two kinds of copper interconnect fabrication are extensively applied in in-

terconnects and metal bumping: Cu-electroplating and Cu-electroless deposition, respectively. Cu-electroless deposition is a method to deposit Cu directly on the barrier layer such as Ta, TaN, Ti, TiN, W, NiB, or AlN (Refs. 13–19) by sensitization, activation, and a replacement process that possesses film characteristics analogous to Cu-electroplating; but its chemical and physical properties are still not superior to Cu-electroplating. Recently, a variety of liner materials as a conductive layer and barrier layer for direct Cu-electroplating were examined, including Pt, Pd, Ru, Os, and Ir, where the formation enthalpy of the metal oxide is smaller than that of Cu oxide.^{20–24} Among these materials, Ni bears low electrical resistivity and high thermal stability, and it has a potential compatible with conventional silicon complementary metal-oxide semiconductor (CMOS) manufacturing. However, it is rarely used as a direct Cu-electroplating template material because of its inherent passive film exposure to air. If nickel's inherent passive film can be overcome using a pretreatment, then it will be a superior candidate for direct Cu-electroplating. In this paper, Ni will be used directly as a Cu-electroplating template to fabricate Cu film and mixed-metal periodic arrays. The material characteristics, the mechanism of adjustable silt width, midinfrared reflectance, and surface hydrophobicity will be investigated.

II. EXPERIMENT

The substrates in our experiments were (100)-oriented p-type wafers, and all substrates were cleaned in a piranha bath (30% H₂O₂ mixed in a 1:3 ratio with concentrated H₂SO₄ at 120 °C followed by coating with 400 nm SiO₂

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(thermal oxides) as a dielectric layer and 50 nm Ni as a direct Cu-electroplating conductive layer. The SiO₂ was deposited by horizontal furnace at 980 °C. The Ni film was sputtered on the SiO₂ using metal-physical vapor deposition (PVD) (MRC Primus 2500 TM) based on 5×10^{-7} torr base pressure, 2 mtorr process pressure, 8 kW dc power, 150 SCCM Ar (SCCM denotes cubic centimeter per minute at STP), and 12 in. Ni target as-sputtered material. The resistivity of as-deposited Ni is 4.85 $\mu\Omega$ cm. Except for depositing Ni film, fabricated three periods of Ni arrays on SiO₂ repeated over the entire 6 in. wafer as a cathode template to construct a mixed-metal array, including 1.05, 1.2, and 2.1 μ m lattice periods, where the line widths are 0.7, 0.8, and 1.4 μ m, separated by SiO₂ widths (slit width) of 0.35, 0.4, and 0.7 μ m, respectively. The Ni arrays was fabricated by conventional optical lithography, followed by a high-density plasma-etch tool (Anelva ILD-4100 helicon wave etcher) using 2300 W rf power, 230 W bias, 90 SCCM Cl₂, and 10 SCCM N₂. The photoresist was removed by acetone to avoid damaging the Ni surface after dry etching. Nickel oxide (NiO) must be removed prior to electroplating. The cathode-coated Ni film and Ni arrays were immersed into dilute H₂SO₄ (98%) for 30 s, which used a mixture of [H₂SO₄]:[H₂O]=1:9 to remove native oxide. Then, the cathode was immediately rinsed with de-ionized water to prevent it from oxidizing again. Note that greater immersion time in H₂SO₄ will tend to damage the Ni surface and lift-off the Ni arrays from SiO₂. The basic three-additive electroplating formulations were used in this paper, formed by mixing 80 g/l CuSO₄, 200 g/l H₂SO₄, 80 g/l HCl, and some additives, such as accelerators, suppressors, and levelers. The semiauto electroplating equipment was applied to deposit Cu on Ni film and Ni arrays, and the area of cathode electrode was 6 in. wafer. The electroplating conditions were 25 °C, 0.44 mA/cm² for a constant current density, and a flow rate controlled at 10 l/min.

The morphology of Cu film and mixed-metal arrays were examined and evaluated by scanning electron microscopy at 15 kV (SEM) (JEOL JSM 6500-F) and atomic force microscopy (AFM) (Veeco multi-mode scanning probe microscope). The AFM tip was N⁺-silicon produced by Nano Sensors, 4 μ m thick, 125 μ m long, 30 μ m wide, 10–15 μ m in tip height, 204–497 kHz resonance frequency, and probe curvature radius <10 nm. The crystal structure and orientation of the deposited Cu was determined by grazing incidence x-ray diffraction (GIXRD) using Cu *K* α radiation (λ = 1.5405 Å) with a Philips X'Pert system, which was operated at 45 kV and 40 mA, and recorded at a scanning rate of 0.02°/s with 2θ range from 35° to 80°.

Fourier transform infrared spectroscopy (FTIR) spectra were measured using a nitrogen-purged spectrometer with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Spectra were obtained with a specular reflectance accessory using polarized light incident perpendicular to the sample. All spectra were referenced against an unmodified

gold film. The range of infrared wavelength is 1.4–10 μ m, and the unpolarized, *S*-polarized, and *P*-polarized reflections were all measured.

Equilibrium contact-angle measurements were made using a KRÜSS GH 100, using 3 μ l drops of de-ionized water dropped onto the sample from a microsyringe. The water drop needs to slightly touch the surface to detach the drop. A picture of the drop was taken a few seconds after the drop stabilized. The contact angle was determined by the classic Young's equation with a Young–Laplace fitting curved around the drop,²⁵ and the value of the contact angle is the average of measurements.

III. RESULTS AND DISCUSSION

A. Characterization of morphology and crystallization

Cu deposition on Cu or Au conductive layers using the electroplating method has the advantages of being convenient, fast, and stable for semiconductor interconnects and package bumping. The lower affinity on solid surface with water generally can be defined by high contact angle; however, the as-deposited Cu conductive layer has a higher contact angle of 62°. Increasing the affinity of electrolyte with the Cu or Au conductive layer is an essential; it enhances the electrolyte to spread on the surface by adding more surfactants. Lower-affinity conductive material with electrolyte is also taken into consideration, exclusive of adding more surfactants. In this paper, the Ni is used as a conductive layer for Cu electroplating. The as-deposited Ni reveals a water contact angle of 16°, and it decreases to 8° by pretreatment in H₂SO₄ immersion to remove the native oxide (not shown here). Regardless of water or electrolyte, they exhibit lower contact angle and hydrophilic property on Ni than on Cu, which reduces the addition of surfactants. The small lattice-constant mismatch is necessary to direct-deposit Cu on Ni with similar crystal structures. Cu and Ni are both face-centered cubic (fcc) structures, and the lattice constant of Cu is 3.61 Å, close to Ni's 3.52 Å. This represents a 3% lattice-constant mismatch, which is significant relative to epitaxy and ensures the same crystallographic orientation of Cu deposited on Ni. To effectively control the morphology and structure of Cu deposited on Ni, we need to explore the growth mechanism. Figure 1 shows the size and distribution of Cu particles deposited on Ni with varying deposition time. The deposition conditions were controlled at 0.44 mA/cm² current density and 10 L/min flow rate. Lower deposition time produces a smaller particle size of around 100 nm due to the initial nucleation mechanism, and the size distribution of particles are uniform across the film, as shown in Fig. 1(a). Increasing the deposition time from 50 to 120 s, the small particles grow gradually from 200 to 400 nm, as shown in Fig. 1(b). In Fig. 1(c), many shapes of Cu particles have formed, such as triangles, rods, and irregular shapes for longer deposition times. Figure 1(d) exhibits various sizes and shapes of particles simultaneously, resulting from sustained nucleation and nuclei growth. The Cu particles eventually precede lateral and vertical growth to construct Cu

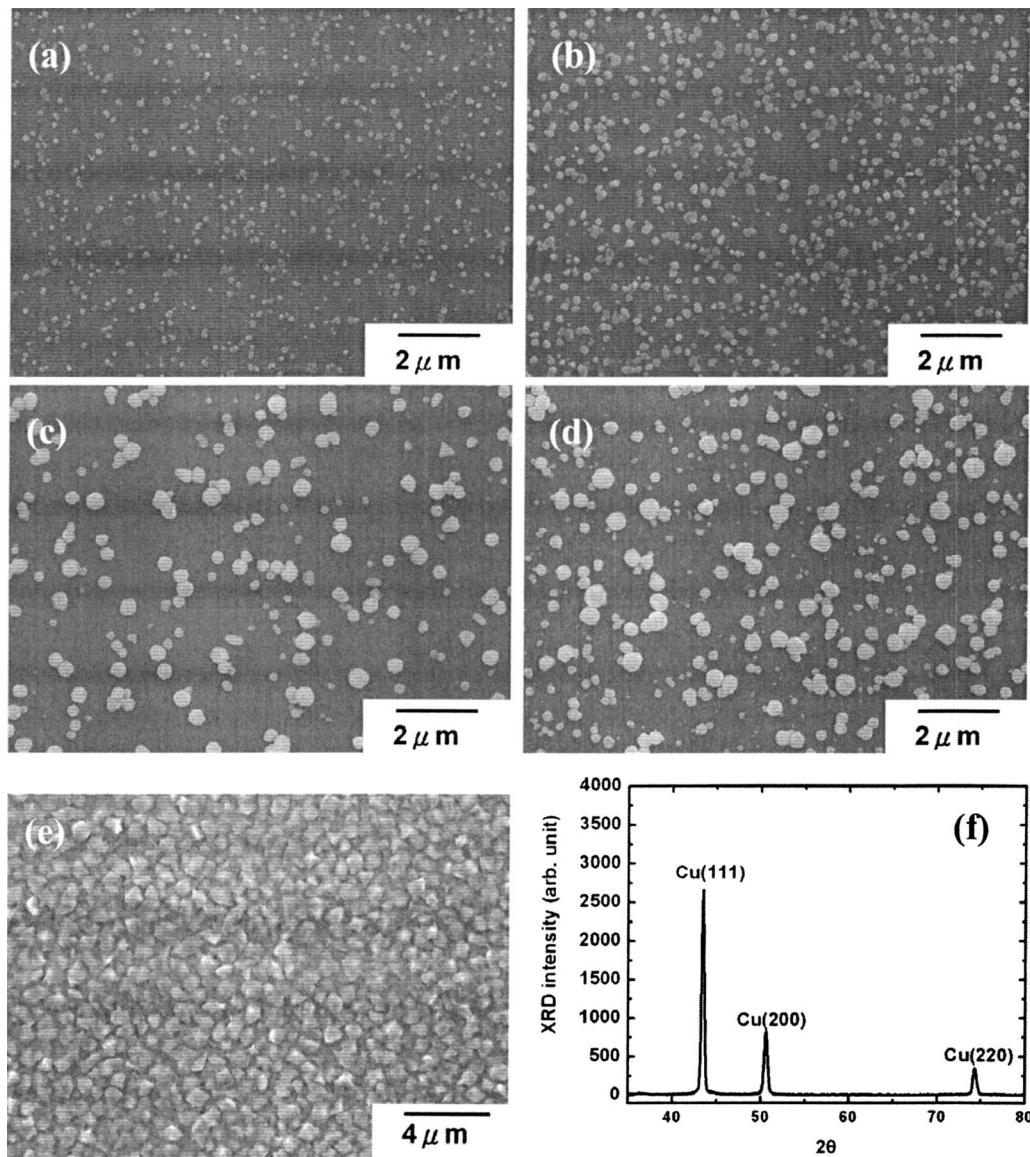


FIG. 1. SEM plane views of Cu deposited on Ni film at different deposition conditions: (a) 20 s, (b) 50 s, (c) 120 s, (d) 300 s, (e) 1200 s, and (f) XRD θ - 2θ plots measured from a Cu film on Ni surface by grazing incidence; diffraction angle $2\theta=43.3^\circ$ for Cu(111), $2\theta=50.4^\circ$ for Cu (200), and $2\theta=74.2^\circ$ for Cu (220).

film on Ni. Figure 1(e) shows the Cu film deposited on Ni after 1200 s, and the large grain-size around $1\ \mu\text{m}$ demonstrated the growth of small grain size apparently. XRD was used to investigate phase structure and crystal orientation. Figure 1(f) shows an XRD pattern of the Cu film deposited on Ni, and all the intense XRD peaks were compared with those at the same positions as the polycrystalline Cu standard in the X'PERT software database. The peak intensity of Cu on the Cu conductive layer was greater than that on the Ni conductive layer, which originated from 3% lattice-constant mismatch, but the crystalline structure of Cu on Ni surface still can be obtained. No oxides or other Cu compounds are observed, indicating that the crystalline structure is pure Cu phase. There are three Cu peaks in the XRD pattern with the strongest at the (111) crystal plane and the other two weaker peaks at (200) and (220), which indicates that a Cu film with

fcc crystalline structure was fabricated. Stronger (111) could be deduced as a preferred growth direction because it has the advantages of low resistivity and high electromigration resistance applied in semiconductor interconnects; periodic Cu lines can also be applied for optical application in advanced.

Figures 2–4 show that the Cu deposited on Ni varies on different periodic arrays as templates that have lattice periods of 2.1, 1.2, and $1.05\ \mu\text{m}$, respectively. The electroplating was controlled at the same deposition conditions as depositing on the Ni film. To explore the influence on the various line width of the Ni arrays, we used Ni line widths of 1.4, 0.8, and $0.7\ \mu\text{m}$ separated by SiO_2 widths of 0.7, 0.4, and $0.35\ \mu\text{m}$, respectively, to investigate the Cu grown on different Ni-array features. Figure 2 shows the plane views of the Ni-array template with deposition times from 20 to 300 s, which has a Ni period of $2.1\ \mu\text{m}$, slit width of $0.7\ \mu\text{m}$, and

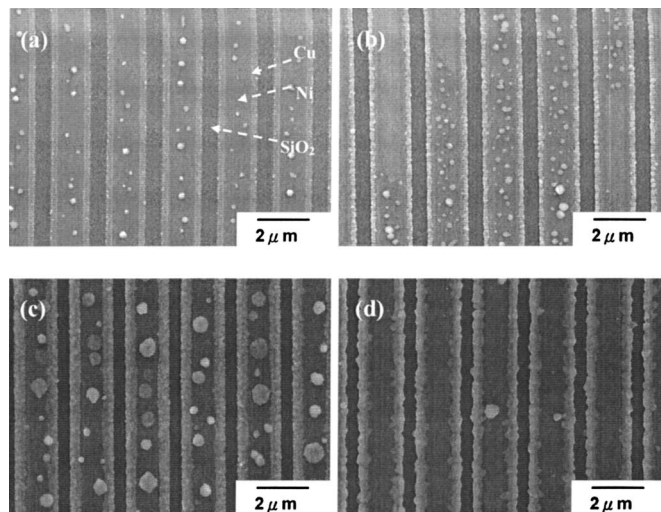


FIG. 2. SEM plan views of Cu deposited on Ni-array template of $2.1\ \mu\text{m}$ period at different deposition conditions: (a) 20 s, (b) 50 s, (c) 120 s, and (d) 300 s. (The template period of Ni array is $2.1\ \mu\text{m}$, which has a $0.7\ \mu\text{m}$ slit and $1.4\ \mu\text{m}$ line.)

line width of $1.4\ \mu\text{m}$. In Fig. 2(a), we see that the initial deposition occurs at the periphery of the Ni line, and it gradually expands inward to the center, which may be attributed to two reasons: First, a dislocation, step, and kink at the periphery caused by the attack of Cl_2 and N_2 during etching, and second, it results from edge effects on the current density and overvoltage. The current is primarily introduced from the edge of the 6 in. wafer into the Ni line to bring about higher resistance and overvoltage due to small line feature. In addition, the Cu particles also grow on the Ni area, where the site is from the as-deposited Cu edges of Ni line to the center, and the various particle sizes are in accordance with the sizes shown in Fig. 1. The crystalline structure of Cu

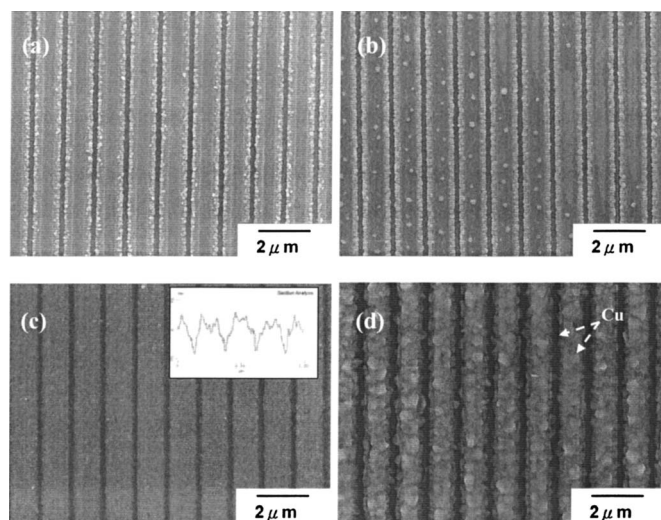


FIG. 3. SEM plan views of Cu deposited on Ni-array template of $1.2\ \mu\text{m}$ period at different deposition conditions: (a) 20 s, (b) 50 s, (c) 120 s, and (d) 300 s. (The template period of Ni array is $1.2\ \mu\text{m}$, which has a $0.4\ \mu\text{m}$ slit and $0.8\ \mu\text{m}$ line.) The inset in Fig. 3(c) is an AFM cross-section linescan analysis.

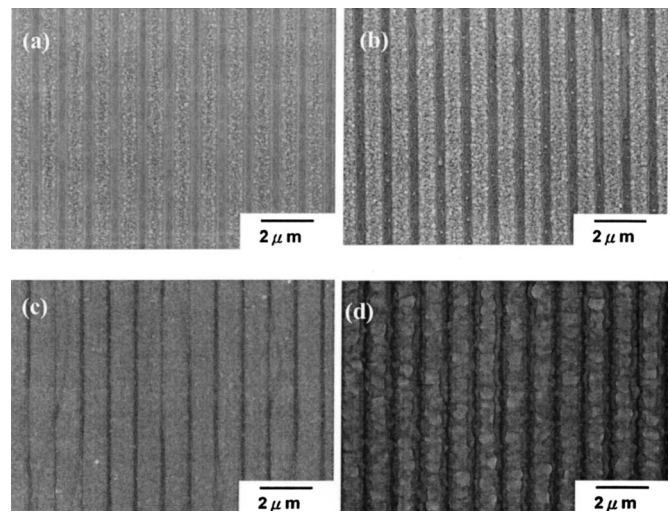


FIG. 4. SEM plane views of Cu deposited on Ni-arrays-template of $1.05\ \mu\text{m}$ period at different deposition conditions: (a) 20 s, (b) 50 s, (c) 120 s, and (d) 300 s. (The template period of Ni array is $1.05\ \mu\text{m}$, which has a $0.35\ \mu\text{m}$ slit and $0.7\ \mu\text{m}$ line.)

deposited on the edges of Ni line is also demonstrated to exist by four peaks (not shown here), Cu(111), Cu(200), Ni(111), and Ni(200), ranging from 2θ of 35° – 60° by GIXRD, which yield at 43.3° , 50.4° , 44.7° , and 52.2° , respectively. These peaks explained the polycrystalline Cu to deposit on Ni line significantly. The slit width is shrunk because of the lateral growth on the edges of the Ni line after a 120 s deposition, as shown in Figs. 2(b) and 2(c), and the shrinkage of slit width is from 0.7 to $0.45\ \mu\text{m}$ after a 300 s deposition, as shown in Fig. 2(d). This result indicates that careful adjustment in lateral growth would be an easy method for controlling the variation in slit width, and the method can easily fabricate various Cu–Ni–Cu– SiO_2 periodic arrays. Obviously, the slit will be covered by depositing Cu with greater deposition time before the wider Ni line ($1.4\ \mu\text{m}$) is covered completely by Cu. Therefore, fully Cu covered on Ni line and slit shrinkage presumably will anticipate to be achieved simultaneously if the array period and Ni line dimension could be reduced.

Figure 3 shows that the plane view of a periodic Ni array of $1.2\ \mu\text{m}$, slit width of $0.4\ \mu\text{m}$, and line width of $0.8\ \mu\text{m}$. The initial growth behavior is similar to the lattice period of the $2.1\ \mu\text{m}$ feature. The slit width is reduced from 0.4 to $0.2\ \mu\text{m}$, shown in Figs. 3(a) and 3(b). Interestingly, the Ni line is fully covered by Cu after a 120 s deposition without further reducing the slit width, as shown in Fig. 3(c). To understand the growth priority at different sites of the line sidewall, the inset in Fig. 3(c) shows the AFM cross-section linescan analysis that indicates the growth is dominated at the lower site of the line sidewall, has a tendency toward constructing Cu– SiO_2 –Cu arrays with a V-shaped channel, and forms a nanoscale mixed-metal slit. Therefore, by increasing deposition time to 300 s, the lateral growth fully covered the slit to reconstruct Cu–Cu arrays instead of Cu– SiO_2 –Cu arrays, which results in broadening the slit again, shown in Fig. 3(d). Hence, we inferred that fully cov-

ered Cu–SiO₂–Cu-array structures with a V-shaped nano-scale slit could be fabricated without sealing the slit by controlling deposition time between 50 and 120 s. To examine the influence of a narrower Ni line on Cu-electroplating, Fig. 4 shows plane views of Cu covering a Ni-array template, which has a period of 1.05 μm , slit width of 0.35 μm , and line width of 0.7 μm . In these figures, we see that the selective Cu deposition on the Ni arrays can be achieved without depositing on SiO₂ areas. Comparing Fig. 4(a) with Fig. 4(b), the Cu particle distributive density and grain size increase with increasing deposition time. In Figs. 4(a) and 4(b), we found that the fully covered Cu on Ni line without altering the slit width at 0.35 μm , which demonstrated that the approximate deposition rate exhibits between the edges and center of Ni line at lower deposition time. The center area predominates slightly over the Cu growth than the edges, while the width of Ni line is less than 0.7 μm . That result can be elucidated by the difference in voltage effect in smaller feature; however, the V-shaped slit can still be obtained. The smaller pattern greatly influences the predominance of Cu growth at specific sites of Ni line. Increasing the deposition time to 120 s as shown in Fig. 4(c), we see that the slit rapidly shrinks from 0.35 to 0.1 μm , and nearly closes the slit with the Cu–SiO₂–Cu structure forming, indicating similar growth behavior to that of Figs. 3(a) and 3(b). The structure reforming is also observed after a 300 s deposition that forms the Cu–Cu grooving structures in Fig. 4(d). In conclusion, we confirmed that combining Cu electroplating with the Ni-array template can fabricate three types of arrays of Cu–Ni–Cu–SiO₂, Cu–SiO₂–Cu, and Cu–Cu, and can adjust slit width simultaneously depending on controlling the deposition time. This method has the great advantage of selectively covering Cu on the narrower Ni array and fabricating a two-step metal array on the broader Ni array based on silicon oxide. The method fabricates directly on 6 in. wafers and is perfectly compatible with CMOS manufacturing without changing the existing process, which is another advantage.

B. Infrared optical behavior of Cu–Ni–Cu–SiO₂ array

The nanoslit periodic metal array performed characteristic concentration and channeling of light in the visible to near-infrared range; however, we will focus on the reflectivity of Cu–Ni mixed arrays from 1.4 to 10 μm to investigate the specific optical behavior. Our approach is particularly suited for low-cost and water-repellent infrared filters due to Cu–Ni mixed-grating by conventional optical lithography, and all materials are compatible with silicon CMOS manufacturing. It is well-known that reflectivity from the metallic lamellar grating is high for *S*-polarized light because of waveguide-cutoff attenuation,²⁶ as shown in Fig. 5. The reflection gradually decreases as wavelength become shorter, which may be attributed to two reasons. First, the wavelength is near the cutoff wavelength of ~ 1 μm . Second, the absorption of Ni becomes more obvious in shorter wavelengths. For reflection spectra of the sample of 300 s Cu-electroplating on the Ni array, two reflection dips occur in the *P*-polarized light at ~ 2

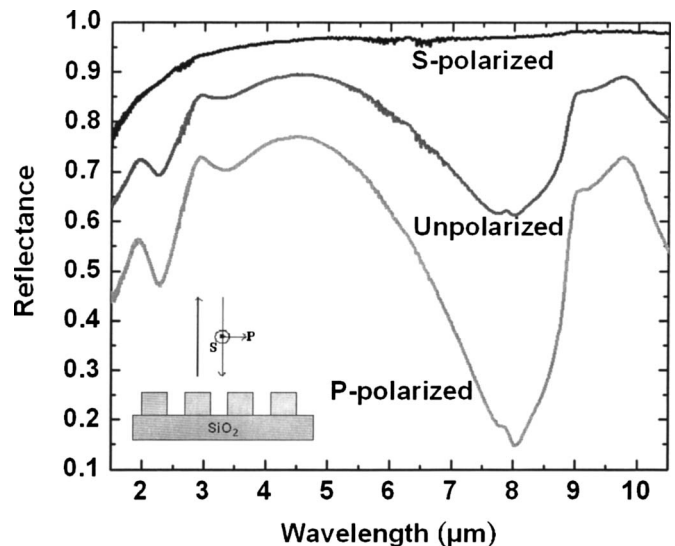


FIG. 5. The reflective spectrum of unpolarized, *S*-polarized (0°), and *P*-polarized (90°) section for 300 s of Cu electroplating on 2.1 μm periodic Ni array.

and ~ 8 μm . This phenomenon may stem from the excitation of surface electromagnetic modes, which can absorb the energy of incident light and re-emit it.²⁷ The dip near 2.2 μm is referred to as the zero-order transmission for the *P*-polarized light because of the coupling to surface plasmon polaritons. These appear at wavelength $\lambda_{\text{sp}} = (d/m) \{ \text{Re}[\epsilon/(\epsilon+1)] \}$ for normal incidence,²⁸ where m is a nonzero positive integer, and ϵ is the dielectric constant of Cu. In the midinfrared range, λ_{sp} is ~ 2.2 μm for $m=1$. On the other hand, the dip near 8 μm may be caused by a different mechanism, that of waveguide resonance.^{27,29} As the deposition time increases, there is more Cu on the sidewall of the Ni line and the slit becomes narrower. Figure 6 shows that the sample with a narrower slit exhibits higher reflection because the reflectivity of Cu is higher than that of Ni in the wavelength we measured. Note that the bandwidths of the reflection dips became narrower as the slit of grating shrinks. This coincides

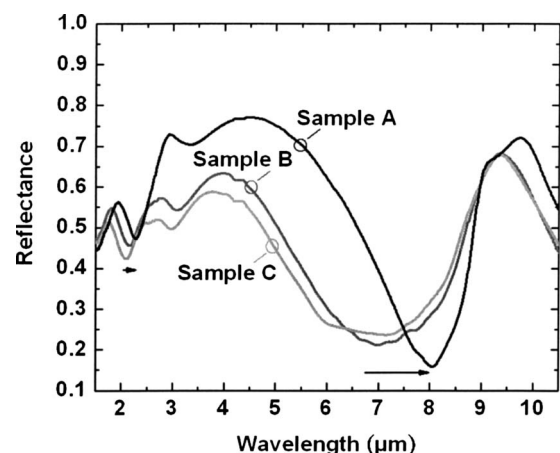


FIG. 6. The reflective spectrum of *P*-polarized section for 300 s (sample A), 50 s (sample B), and 20 s (sample C) deposition time on 2.1 μm periodic Ni array.

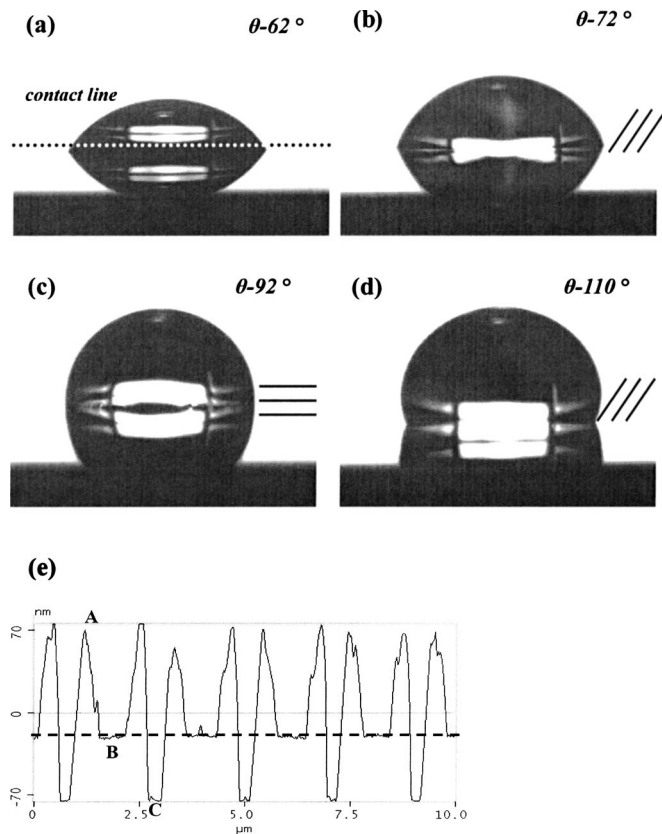


FIG. 7. Behavior of water droplet for 300 s deposition time (a) as-deposited rough copper film on Ni, (b) Ni arrays perpendicular to the three-phase contact line, (c) Cu-Ni-Cu-SiO₂ arrays parallel to the three-phase contact line, and (d) Cu-Ni-Cu-SiO₂ arrays perpendicular to the three-phase contact line, (e) AFM cross-section linescan. [The insets in (b), (c), and (d) are in the direction of periodic arrays with respect to the contact line; the period of the array is based on 2.1 μm].

with the result in Ref. 27. We also found some redshift in the reflection spectra as the slit shrunk but the reason is unclear. We may infer that it is related to the excitation condition of the surface plasmon polarizations for mixed Cu-Ni metals.

C. Characterization of surface hydrophobicity

The surface hydrophobic and hydrophilic properties can be observed through water contact-angle measurement. The hydrophobicity property is determined by altering the surface roughness or surface free-energy with respect to changing the water contact angle. Increasing surface roughness or lowering free-energy can effectively achieve a hydrophobic surface;^{2,30,31} however, to create a superhydrophobic surface, where the water contact angle is greater than 150°, one must increase the surface roughness and lower the free energy of the surface simultaneously. The particular optical property of Cu-Ni-Cu-SiO₂ arrays on 2.1 μm spacing in the midinfrared has been investigated in this paper. Surprisingly, however, it also found that the hydrophobic surface is fabricated on the hydrophilic Ni-array surface while controlling the deposition time under 300 s. Figure 7 shows the contact

angle of the as-deposited Cu film, Ni array, and Cu-Ni-Cu-SiO₂ array. Figure 7(a) reveals the contact-angle variation from 8° (Ni surface) to 62° (Cu surface) on Ni surface caused by its surface chemical property. Figure 7(b) shows the contact angle of 72° on a 2.1 μm Ni array because of surface periodic roughness, which verifies the roughness effect on contact-angle variation. The surface hydrophobicity is enhanced while fabricating periodic Cu-Ni-Cu-SiO₂ arrays on 2.1 μm spacing after 300 s deposition, and the contact angle is greater than 90°. In Figs. 7(c) and 7(d), the water contact angles on the Cu-Ni-Cu-SiO₂ arrays are 92° and 110°, where the three-phase contact lines are parallel and perpendicular to the arrays direction, respectively. To understand the increase in contact angle compared to Ni array, Fig. 7(e) shows the cross-section linescan of Cu-Ni-Cu-SiO₂ arrays by AFM to interpret the behavior. It can be seen that specific two-step periodic structures, Cu-to-SiO₂ and Cu-to-Ni, illustrated that the drop height of A-C and A-B are 150 and 90 nm, respectively. Therefore, higher contact angles could be achieved on this structure due to its nano- and microstructures. We believe that increasing the SiO₂ width and shrinking the line width appropriately will facilitate the surface to create more nano- and microstructures to achieve superhydrophobicity. Furthermore, the difference in water contact angles on Cu-Ni-Cu-SiO₂ arrays between the parallel and orthogonal directions, 20°, is consistent with the results proposed based on silicon groove structure by Yoshimitsu *et al.*²⁵ The interesting behavior can be explained by the water drop facing the different degree of roughness alternation at parallel and orthogonal directions while the drop touched the array's surface. The two-step periodic roughness exhibited in the orthogonal direction with respect to the Ni array and only slight one-step roughness in the parallel direction resulted in the difference of contact angle on the array structure. In addition, the difference in the contact angle also results from the energy gap for the movement of the three-phase contact line. The contact line in the orthogonal direction with respect to periodic arrays displayed discontinuous movement to exhibit higher contact angle than in the parallel direction. Higher contact-angle behavior may be elucidated by Wenzel's model,³² where the space between the protrusions on the surface is filled by the liquid and the basic wetting behavior of a surface is enhanced by roughness or surface texture; the relation is defined as follows:

$$\cos \theta_r = \gamma \cos \theta_f,$$

where θ_r is the apparent contact angle on a rough surface, θ_f is the contact angle of water on a smooth surface of identical chemistry, and γ is the roughness factor, which is defined as the ratio of actual surface area over the projected area. The real roughness factor measured by SEM observation is around 2.5. This is in agreement with the calculated roughness of 2.2 by Wenzel's model. It demonstrated that the hydrophobic behavior of Cu-Ni-Cu-SiO₂ arrays can be predicted by Wenzel's model.

IV. CONCLUSIONS

Combining Cu-electroplating with the Ni-array template has successfully fabricated periodic Cu or Cu–Ni mixed-metal arrays. In addition, the various Cu line widths and slit widths on the Ni array could be controlled depending on the deposition time. The specific Cu–Ni–Cu–SiO₂ periodic arrays exhibit slit-width shrinkage, narrower reflective bandwidth, reflective spectra dips, and redshift in the range of 1.4–10 μm . Furthermore, the hydrophobic property is also observed on the specific Cu–Ni mixed-metal arrays. We have successfully used this approach to manipulate the characteristic midinfrared reflective wavelength and surface hydrophobicity.

ACKNOWLEDGMENTS

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- ¹Z. Yoshimitsu, A. Nakajima, T. Watanabe, and K. Hashimoto, *Langmuir* **18**, 5818 (2002).
- ²N. J. Shirtcliffe, G. McHale, M. I. Newton, G. Chabrol, and C. C. Perry, *Adv. Mater. (Weinheim, Ger.)* **16**, 1929 (2004).
- ³N. J. Shirtcliffe, G. McHale, M. I. Newton, and C. C. Perry, *Langmuir* **21**, 937 (2005).
- ⁴C. E. Moran, C. Radloff, and N. J. Halas, *Adv. Mater. (Weinheim, Ger.)* **15**, 804 (2003).
- ⁵O. Azzaroni, M. H. Fonticelli, G. Benitez, P. L. Schilardi, R. Gago, I. Caretti, L. Vazquez, and R. C. Salvarezza, *Adv. Mater. (Weinheim, Ger.)* **16**, 405 (2004).
- ⁶A. Hozumi, S. Asakura, A. Fuwa, N. Shirahata, and T. Kameyama, *Langmuir* **21**, 8234 (2005).
- ⁷O. Azzaroni, P. L. Schilardi, and R. C. Salvarezza, *Electrochim. Acta* **40**, 3107 (2003).
- ⁸S. Zhong, M. Wang, X. B. Yin, J. M. Zhu, R. W. Peng, Y. Wang, and N. B. Ming, *J. Phys. Soc. Jpn.* **70**, 1452 (2001).
- ⁹P. L. Schilardi, O. Azzaroni, and R. C. Salvarezza, *Langmuir* **17**, 2748 (2001).
- ¹⁰R. Zong, J. Zhou, Q. Li, L. Li, and W. Wang, *Chem. Phys. Lett.* **398**, 224 (2004).
- ¹¹H. Cong and W. Cao, *Adv. Funct. Mater.* **15**, 1821 (2005).
- ¹²I. U. Sxhuchert, M. E. Toimil, M. D. Dobrev, J. Vetter, R. Neumann, and M. Martin, *J. Electrochem. Soc.* **150**, C189 (2003).
- ¹³S. Y. Chang, C. J. Hsu, R. H. Fang, and S. J. Lin, *J. Electrochem. Soc.* **150**, C603 (2003).
- ¹⁴C. H. Yang, W. L. Yang, W. Chang, and W. W. Tseng, *J. Electrochem. Soc.* **153**, C301 (2006).
- ¹⁵R. K. Aithal, S. Yenamandra, R. A. Gunasekaran, P. Coane, and K. Varahramyan, *Mater. Chem. Phys.* **98**, 95 (2006).
- ¹⁶J. J. Kim, S. K. Kim, and Y. S. Kim, *J. Electrochem. Soc.* **151**, C97 (2004).
- ¹⁷Y. S. Kim, D. L. Bae, H. Yang, and H. S. Shin, *J. Electrochem. Soc.* **152**, C89 (2005).
- ¹⁸M. Yoshino, Y. Nonaka, J. Sasano, I. Matsude, Y. Shacham-Diamand, and T. Osaka, *Electrochim. Acta* **51**, 916 (2005).
- ¹⁹H. Yanagimoto, S. Deki, K. Akamatsu, and K. Gotoh, *Thin Solid Films* **491**, 18 (2005).
- ²⁰M. W. Lane, C. E. Murray, F. R. McFeely, P. M. Vereecken, and R. Rosenberg, *J. Appl. Phys.* **83**, 2330 (2003).
- ²¹D. Josell, D. Wheeler, and T. P. Moffat, *Electrochem. Solid-State Lett.* **6**, C143 (2003).
- ²²D. Josell, C. Witt, and T. P. Moffat, *Electrochem. Solid-State Lett.* **9**, C41 (2006).
- ²³D. Josell, J. E. Bonevich, T. P. Moffat, T. Aaltonen, M. Ritala, and M. Leskela, *Electrochem. Solid-State Lett.* **9**, C48 (2006).
- ²⁴Y. S. Diamand, *J. Electron. Mater.* **30**, 336 (2001).
- ²⁵Z. Yoshimitsu, A. Nakajima, T. Watanabe, and K. Hashimoto, *Langmuir* **18**, 5818 (2002).
- ²⁶Z. Li, I. El-Kady, and K. Ho, *J. Appl. Phys.* **93**, 38 (2003).
- ²⁷J. A. Porto, F. J. Garcia-Vidal, and J. B. Pendry, *Phys. Rev. Lett.* **83**, 2845 (1999).
- ²⁸H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Grating* (Springer, Berlin, 1998).
- ²⁹T. López-Rios, D. Mendoza, F. J. García-Vidal, J. Sánchez-Dehesa, and B. Pannetier, *Phys. Rev. Lett.* **81**, 665 (1998).
- ³⁰S. Wang, L. Feng, and L. Jiang, *Adv. Mater. (Weinheim, Ger.)* **18**, 767 (2006).
- ³¹Z. Guo, J. Fang, L. Wang, W. Liu, S. Wang, L. Feng, *Thin Solid Films* **515**, 7190 (2007).
- ³²E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, C. D. W. Wilkinson, and M. O. Riehle, *Nano Lett.* **5**, 2097 (2003).