

## One-step electroless synthesis and properties of copper film deposited on silicon substrate

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Received 3 July 2007, revised 24 March 2008, accepted 3 April 2008 Published online 4 June 2008

PACS 61.43.Gt, 62.20.de, 73.61.At, 81.15.Pq

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A one-step electroless deposition method was developed to synthesize sponge-like copper film with favourable mechanical adhesion on silicon substrate. X-ray diffraction and X-ray photoelectron spectroscopy analysis and field emission scanning electron microscopy observations indicate that the asprepared copper film is polycrystalline and composed of copper nanoparticles with a diameter ranging from 45 nm to 60 nm, the thickness of the film being approximately 2 µm.

**1** Introduction The deposition of metallic structures at a micro-/nanoscale on semiconductor substrates such as silicon wafer has potential application in fabrication of electrical interconnections and microsensors in microelectronics. For instance, copper film deposited on silicon substrate can be used as electrical interconnections ranging from a few nanometres to several micrometres thick [1]. Copper deposition has been developed rapidly recently [2– 8] due to the potential application of copper with low electrical resistivity (~1.72  $\mu\Omega$  cm) in microelectronics and mircrosensors and high elecromigration resistance compared with other metals [9]. Several methods for copper metallization have been studied in previous reports, such as the electroplating method, physical vapour deposition (PVD) and chemical vapour deposition (CVD) [10–13]. However, the costly experimental equipment and critical experimental conditions of the PVD and CVD methods limit large-scale synthesis for industrial applications [14, 15]. Therefore, it would be of interest if a preparation method controlling the crystal forms under mild conditions were developed. Electroless deposition is considered to be a favourable method in the semiconductor industry, be-



deposition has emerged as the method of choice for metallization at present due to its fast deposition speed, good filling capability and good uniformity [16, 17]. However, limitations still remain in electroless deposition; examples are the usage of formaldehyde, which acts as a reducing agent [18, 19], and HF solution, in which the copper can be directly deposited through a redox reaction [20] with sili-

cause of the low processing temperature and the sub-

request for experimental equipment. Especially, electroless

Hydrogen obtained through the reaction of sodium hydroxide

and silicon in ethylene glycol solution was employed to re-

duce in situ the copper ions to form metal copper films on the

silicon substrate. The electrical and mechanical properties of

the as-prepared copper film were measured. The results show

that the as-prepared copper film possesses high resistivity and

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low Young's modulus due to its special structure.

con without the need for reducing agents. Such methods are environmentally hazardous due to the corrosiveness and high toxicity of both formaldehyde and HF. Recently, the deposition of a 50 nm thick layer of copper on silicon without the use of either formaldehyde or HF acid has been reported. This method uses pre-sputtered deposited titanium film, which is less toxic but more costly compared with formaldehyde and HF, as the reducing agent [21]. Therefore, the deposition of copper films on specific substrate via a low-cost, environmentally friendly chemical route is expected to be further developed.

We report in this paper a one-step method for spongelike copper film deposited on silicon substrate with favourable mechanical adhesion via a solvent thermal route, which is considered as a low-cost, non-toxic and mild chemical method for fabricating copper film. The primary principle used in this method is based on the reactivity of silicon under basic conditions. In detail, silicon can react with hydroxide ions to produce hydrogen, by which the cupric ion can be reduced:

$$\operatorname{Si} + 2\operatorname{OH}^{-} \to \operatorname{SiO}_2 + \operatorname{H}_2^{\uparrow} + 2e^{-}.$$
 (1)

The standard electrode potential of copper is 0.3402 V:

$$Cu^{2+} + 2e^{-} \to Cu , \qquad (2)$$

and thus the cupric ion can be deoxidized by hydrogen for which the standard electrode potential is 0 V. So it is conceivable to deposit copper on a silicon surface as long as one controls the experimental parameters, such as the concentration of  $Cu^{2+}$ ,  $OH^-$  and the dispersant, the reaction temperature and so on.

In our study, we successfully deposited sponge-like copper film on silicon substrate using ethylene glycol (EG) as the solvent, cupric nitrate as the  $Cu^{2+}$  source, sodium hydroxide as the OH<sup>-</sup> source and polyvinylpyrrolidone (PVP) as the dispersant. The as-prepared copper film is polycrystalline and has uniformity in thickness. The electric and mechanical properties were investigated. The sponge-like structure is responsible for high electric resistivity and low Young's modulus. To our knowledge, this is the first time polycrystalline copper film has been deposited on silicon substrate via a low-cost, non-toxic and mild chemical route.

**2 Experimental** All the reagents were of analytical purity, purchased from Shanghai Chemicals Company, and used without further purification. The silicon wafer (heavily boron-doped,  $0.003-0.006 \ \mu\Omega \ cm$ , p-type (111) orientation) was pre-treated in sequence with isopropyl alcohol (ultrasonic bath,  $10-15 \ min$ ), NH<sub>3</sub>·H<sub>2</sub>O (25%)/H<sub>2</sub>O<sub>2</sub> (30%)/H<sub>2</sub>O (the ratio was 1:1:5 by volume, 60 °C, 30 min)

and deionized water to remove the impurities on the silicon wafer surface. In a typical procedure, 0.5 g sodium chloride (NaCl) and 0.4 g PVP (K30,  $M_w = 40000$ ) were ultrasonically dissolved in 10 ml EG, and stirred for 10 min to give a transparent viscous solution. After that, 0.05 mmol cupric nitrate (Cu(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 3H<sub>2</sub>O) was added into the solution with constant stirring followed by the addition of 1 ml sodium hydroxide (0.5 mol/l) dropwise. The as-prepared solution together with the pre-treated silicon wafer was transferred into a Teflon-coated stainless steel autoclave with a capacity of 15 ml. The autoclave was maintained at 160 °C for 48 h. After the autoclave cooled to room temperature naturally, it was found that the silicon wafer was covered with bright red surfaces and red-brown powder was on the bottom of the autoclave. The silicon wafer was then taken out of the solution and washed with deionized water and alcohol several times and dried at room temperature.

The silicon wafer was characterized using X-ray diffraction (XRD; Philips X-ray diffractometer with graphite monochromatized Cu K<sub>a</sub> radiation ( $\lambda = 1.54187$  Å)), X-ray photoelectron spectroscopy (XPS; VGESCALAB MKII spectrometer with an excitation source of Mg K<sub>a</sub> = 1253.6 eV) and field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700 FSEM). The resistance of the film deposited on silicon substrate was measured using the standard four-point probe method. The Young's modulus and hardness of the films were determined using a nanoindenter (Hysitron Com. Ms02100601).

**3 Results and discussion** The XRD pattern of the sample is presented in Fig. 1a. Besides the (111), (222) diffraction peaks of (111) orientation silicon wafer (JCPDS 89-5012), the three relatively weaker diffraction peaks can be indexed as the (111), (200) and (220) diffraction peaks of cubic copper with cell constant of 3.612 Å, which is consistent with the values given in the standard card (JCPD-04-0836). No other impurities, such as copper oxide or copper silicate, were detected in the XRD analysis.



Figure 1 (online colour at: www.pss-a.com) a) XRD pattern of the as-prepared copper film prepared at 160 °C for 48 h. XPS spectra of product: b) C 1s; c) N 1s.

It is concluded that the film deposited on the silicon wafer surfaces is composed of phase-pure copper. In addition, according to the 1.11 intensity ratio of the first/second strongest diffraction peak  $(I_{111}/I_{200})$  for bulk Cu [22], the intensity ratio of  $I_{111}/I_{200}$  in the XRD pattern is about 2.3.

The co-deposition phenomenon of other substances can be demonstrated by high-resolution XPS. The co-deposition of PVP is confirmed by the XPS spectrum of C 1s (Fig. 1b). The C 1s spectrum is composed of four peaks and the binding energies of these peaks are 284.6 eV (C–H bonding), 286.0 eV (C–C bonding), 287.7 eV (C–N bonding) and 289.0 eV (C–C bonding). These binding energies can be attributed to four types of carbon atoms in PVP [23]. The co-deposition of  $NO_3^-$  is confirmed by the XPS spectrum of N 1s (Fig. 1c). There are two nitrogen contributions in the N 1s core level spectrum: the binding energy centred at 401.9 eV can be assigned to C–N bonding in PVP while the binding energy centred at 411.1 eV can be assigned to  $NO_3^-$  adsorption.

The morphology of the copper film is presented in Fig. 2. Figure 2a shows the representative morphology of the film, which appears smooth and homogeneous. Figure 2b shows a magnified FE-SEM image of the film. The film is composed of loosely stacked copper nanoparticles 45-60 nm in size. With more careful observation, it can be seen that some particles aggregate together to form larger nanoblocks. Figure 2c shows a low-magnification FE-SEM image of the cross-section of the film. The film has uniformity in thickness and attaches to the substrate closely. Figure 2d shows a magnified cross-sectional image of the film, from which the tri-layered structure can be observed clearly. The three layers from the top down are sponge-like copper film, copper-silicon interface area and silicon substrate, respectively. The average thickness of the copper film was calculated as approximately 2.2 µm.



**Figure 2** a) Representative FE-SEM image of the surface morphology of copper film deposited on silicon substrate; b) magnified image of the film; c) representative FE-SEM image of the cross-section of the same copper film; d) magnified image of the cross-section showing the tri-layered structure.

The above results indicate that the sponge-like copper film was formed at the copper–silicon interface area. On the basis of the data, a possible mechanism for the formation of the sponge-like copper film and the rough erodelike surface of the silicon wafer can be tentatively proposed. The formation process is illustrated in Scheme 1. In the first step, with hydroxide ions adsorbed on the surface of the wafer (Scheme 1, step a), the reaction between silicon and hydroxide ions occurs on the surface of the wafer (Eq. (1)). The dissolution of silicon dioxide in solution is responsible for the formation of the copper–silicon interface:

$$\operatorname{SiO}_2 + 2\operatorname{OH}^- \to \operatorname{SiO}_3^{2-} + \operatorname{H}_2\operatorname{O} . \tag{3}$$

In the second step, the hydrogen atoms formed which have strong reducing ability. It is quite easy to reduce the Cu(II) ions. The continuous formation of copper deposited on the substrate surface consists of three steps. First, the copper ions interact with PVP. Second, copper ions exposed to the hydrogen atmosphere are reduced to copper atoms on the surface of the silicon substrate, and then nearby copper atoms aggregate at close range to form the primary nanoparticles (Scheme 1, step b). Finally, the primary nanoparticles interact with PVP deposited on the silicon substrate, some of which coalesce with other nearby primary nanoparticles to form large aggregates (Scheme 1, step c). The powder on the bottom of the autoclave may be a result of the reaction between copper ions and hydrogen atmosphere which diffuses to the solution. For the two reasons that the copper nanoparticles interact with PVP and the rough surface morphology of the substrate, the as-prepared copper films formed by the deposition of copper nanoparticles are not compact and possess special sponge-like structures (Scheme 1, step d). And then the copper film deposited on the silicon substrate is formed (Scheme 1, step e). During the whole deposition process, PVP is expected to inhibit the further aggregation of copper nanoparticles [24] and NaCl slows down the deposition speed of copper [25].

To investigate the mechanical and electric properties of the as-prepared copper film, the Young's modulus and electrical resistance of as-prepared sample was measured using nanoindentation and four-probe measurements, re-



**Scheme 1** Formation process of the copper film deposited on silicon substrate.

location	$h_{\rm c}({\rm nm})$	$P_{\rm max}$ (µN)	$E_{\rm r}$ (GPa)	H (GPa)
1	424	223	0.58	0.040
2	451	205	0.29	0.033
3	461	274	1.01	0.042
4	474	174	0.83	0.026
5	514	257	0.42	0.032
6	653	233	0.24	0.019
7	751	282	0.78	0.017
8	769	276	0.52	0.016
9	870	245	0.18	0.011
10	948	234	0.16	0.0093
11	1013	191	0.27	0.0067
12	1167	319	0.28	0.0059
average value	708	243	0.46	0.021

**Table 1** Plunge depth ( $h_c$ ), force ( $P_{max}$ ), Young's modulus ( $E_r$ ) and hardness (H) values of the copper film (at different locations).

spectively. The submicrometre nanoindentation of thin films on substrates is a common method to measure the Young's modulus and hardness [26, 27]. After the loaddeflection and unload-deflection curves were obtained by the nanoindenter, the Young's modulus and hardness values could be determined by fitting the experimental curves through the nanoindenter software. As shown in Table 1, the set of Young's modulus values obtained for the copper film (at different locations) exhibits a scatter showing that the film is not compact and homogeneous. The average value of Young's modulus of the copper film is approximately 0.46 GPa, which is much lower than the value of bulk polycrystalline copper (130 GPa), bulk copper film reported by Jamting et al. [28] and copper films prepared through various methods. For example, Read [29] measured electron-beam deposited and sputtered copper film using a nanoindenter, and the Young's modulus was 99 GPa and 109 GPa, respectively, and Farhat et al. [30] reported a Young's modulus of  $102.46 \pm 2.5$  GPa of as-sputtered copper film by the nanoindentation method. The special sponge-like structure of our prepared copper film plays an important role in the decreased Young's modulus and hardness values and leads to little regularity between plunge depth  $(h_c)$  and plunge force  $(P_{max})$ .

Due to the relatively large thickness of the as-prepared film (2.2 µm) which is far larger than the mean free path (MFP) of copper (39 nm), a body transport mechanism should be applied, so the resistivity can be calculated using the formula  $R = \rho l/s$  (where *R* is resistance, *l* is the length between the inner contacts and *s* is the cross-sectional area). Figure 3 displays the temperature dependence of electrical resistivity ( $\rho$ ) of the copper film. It has a value of 950 µ $\Omega$  cm at room temperature, decreasing linearly with on cooling from 300 to 50 K. Below 50 K, it gradually saturates to a value of about 625 µ $\Omega$  cm at 0 K. Electrical resistivity of a pure metal at low temperatures can be represented by the formula

$$\rho = \rho_0 + JT^k , \qquad (4)$$



**Figure 3** Resistivity of copper film as a function of temperature from 15 to 300 K.

where  $\rho$  is the measured electrical resistivity,  $\rho_0$  is the residual resistivity and J and k are constants [31]. Usually,  $\rho_0$ is dependent only on the amount of impurities and defect concentration in pure metals. In our work, due to many voids existing in the copper film, the value of  $\rho_0$  got to 650  $\mu\Omega$  cm. After subtracting  $\rho_0$ , the room temperature electrical resistivity of the copper film is about 300  $\mu\Omega$  cm, which is still significantly higher than that of bulk copper  $(1.72 \ \mu\Omega \ cm)$  and other films prepared by different methods, such as  $32.34 \pm 0.50 \ \mu\Omega$  cm of 11.5 nm thick copper film thermally evaporated onto  $\sim 500 \text{ nm}$  thick SiO<sub>2</sub> on Si(100) substrate [32] and 22  $\mu\Omega$  cm of 11 nm thick copper film deposited by ion beam deposition [33]. The electrical resistance in a metal thin film arises due to electron scattering by phonons, point defects, impurities, grain boundaries, film surfaces and interfaces. First of all, the contact resistance of nanoparticles maybe very high due to their partial embedding in PVP impurities, which was demonstrated by XPS analysis. Also, the thickness of the as-prepared sample (2.2 µm) is larger than the MFP of copper (39 nm). And surface and interface scattering needs to be considered in the increase of the resistivity of the copper film. Electron scattering originating from grain boundaries would result in the increase in resistivity of the copper film. The existence of a large amount of pores in the film leads to a decrease of the efficient cross-sectional area of copper which notably increases the resistivity of the copper film. Moreover, the existence of many nanopores the width of which is very small can also result in increased width of the conducting paths, which is one of the reasons causing the high resistivity. In general, the special sponge-like structure of the copper film leads to the high electrical resistivity which is different from samples prepared by other deposition methods.

**4 Conclusions** In this paper we have developed a one-step deposition method to prepare copper films on silicon substrates. Our results indicate that the as-prepared copper film has a sponge-like structure, about 2.2  $\mu$ m thick

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and composed of polycrystalline copper nanoparticles. Due to its special sponge-like structure, the as-prepared copper film possesses higher resistivity (300  $\mu\Omega$  cm) and lower Young's modulus (0.46 GPa) than bulk copper and the films prepared by other methods. The preparation of more compact and homogeneous films having lower electrical resistivity will be the focus in our future work. It is also expected that these copper films may have potential applications in microelectronics, not only for the requirement of mild reaction conditions, but also for extension to other metals such as silver, platinum and so on to deposit on the silicon substrate.

**Acknowledgement** This work was supported by the National Natural Science Foundation of China.

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