Preparation of copper thin film mask by sputtering technique assisted by polymer mask photolithography

C Pakpum¹,²
¹Program in Applied Physics, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand
E-mail: chupong@mju.ac.th

Abstract. This research aims to build cheaply homemade DC magnetron sputtering system for deposit metal thin films on substrate by assist of polymer mask photolithography. The metal thin film is able to use as a hard mask for patterning transfer via chemical wet etching or plasma dry etching process and it also can be used as a metal electrode in micrometre scale. Prepared copper thin films will be measured thickness by scanning electron microscope. Crystalline structure of the thin films will be examined by x-ray diffractometer. Elemental analysis contained in the films will be determined by energy dispersive x-ray spectrometer and morphology of the films will be revealed by scanning electron microscope.

1. Introduction
Many methods of metal thin film deposition processing techniques have been conducted for obtaining high quality of deposited film in conjunction with low cost of mass production. Investigated deposition techniques, up to now, composed of; direct current (DC) sputtering, radio frequency (RF) sputtering, thermal evaporation, electron beam physical vapour deposition, radio frequency (RF) ion plating, ultrasonic spray pyrolysis, wet chemical sol-gel process, chemical vapour deposition (CVD) and plasma enhanced chemical vapour deposition (PECVD). By comparison, DC sputtering has been considered as a process of choice providing good uniformity of large scale processing substrates and providing acceptable deposited thin films quality as well [1]. In fundamental, sputtering phenomena occurred from positive ions, exist in plasma that generated from collision process by energetic electrons gained energy from dense electric field between two electrodes supplied by DC high voltage in vacuum chamber, to bombard atoms on surface substrate called “target” (which generally placed on electrode that applied by negative voltage) resulted in removing atoms on target to deposit on another substrate surface called “substrate” placed on electrode that having higher electric potential eventually atoms from target accumulate on substrate to form the films [2]. The traditional process of polymer photolithography to create polymer patterns on silicon substrate were achieved by sequence of three steps process; coating light-sensitive polymer on substrate, irradiating ultraviolet (UV) light to polymer through the desired pattern (photo-mask) and chemical wet etching to UV exposed polymer. The cured portion by UV of polymer cause that part hardened and can withstand to chemical wet etching, eventually the polymer layer on substrate appeared the same pattern with photo-mask [3]. In this work, author aims to build cheaply homemade DC magnetron sputtering system for deposit copper (Cu) thin films on silicon (100) substrate by assist of polymer mask photolithography by means of the polymer mask will be used as a temporary mask to allow sputtered Cu atoms to deposit on silicon substrate area where dry film mask was unprotected. Prepared copper thin films will be
measured thickness by scanning electron microscope. Crystalline structure of the thin films will be examined by x-ray diffractometer. Elemental analysis contained in the films will be determined by energy dispersive x-ray spectrometer and morphology of the films will be revealed by scanning electron microscope.

2. Experimental methods

2.1. Fabricate homemade DC magnetron sputtering system

![AC to DC circuit diagram](image)

**Figure 1.** Illustrate AC to DC circuit (left) and performance to generate DC output (right).

In Figure 1 on left side, showed AC to DC circuit used to produce plasma in vacuum chamber while input voltage is AC (0-230 volts) and transformed to negative DC high voltage output at points where multimeter connected shown in the figure. After test the circuit, in Figure 1 on right side, with 20 volts (AC) input to the circuit results output 250 volts (DC) therefore this circuit should provide maximum 3,105 volts DC output while applying maximum AC input at 230 volts.
In Figure 2 on left side, showed the system was constructed by using a parallel of grounded iron electrode and cathode copper electrode used to ignite the plasma, plasma glow discharge is illustrated on the right side of Figure 2. An electric potential, generated from direct current, of a few hundred to several thousand volts is applied between the two electrodes causing strong electric field built-up between electrodes, a partial of neutral atoms in the process chamber is ionized by collision of energetic electrons (which move in a distance enough to gain kinetic energy from electric filed) that driven moving downward to electrode that bias with a negative voltage and in coupled with moving along magnetic field lines (that generated by the permanent magnets mounted on the back side of the copper electrode) in corkscrew pattern, while ions that generated from collision will move in opposite direction of electrons that are moved to grounded electrode in upward direction. The interaction of ions to electric fields increases the degree of ionization to the neutral gas (N2 molecules and O2 molecules residue in vacuum chamber) by collision process. It is not clear understanding of dissociation and ionization process of N2 plasma yet, due to the participation complicated processes by the interaction of; molecular vibration process, electron vibration process, chemical process and surface kinetic process. Explanation of the reactivity of N2 molecules contained in plasma may play a major role by molecules excitation by vibration process and charge-exchange processes (metastable states) [4]. To dissociate N2 molecule generally required energy of about 9.756 eV [5] and such this amount of energy possible supply by electron collision process in low pressure circumstance comply in equation (1) and (2). In addition, vibrational dissociation and dissociative recombination according to equation (3) [6] are also possible;

\[
\begin{align*}
N_2 + e^- & \rightarrow N^+ + N + 2e^- \quad (1) \\
N_2 + e^- & \rightarrow N_2^+ + e^- \quad (2) \\
e^+ + N_2^+ & \rightarrow N + N \quad (3)
\end{align*}
\]

2.2. Sample preparation

The (100) oriented p-type (1-40 Ω·cm) of 3-inch diameter single-side polished silicon (Si) wafer was cut to small pieces. To deposit patterned Cu thin film on Si surface, the Si pieces were processed with a conventional photolithography process; laminated with polymer dry film photoresist, UV exposure by using desired patterned mask and mask development by sodium carbonate developer. After that, the sample was put on the iron electrode at the position that on top of the hole at the center of iron electrode, by facing the patterned dry film down to the Cu electrode so that the unprotected Si surface from cured UV dry film will be deposited by sputtered Cu atoms from Cu electrode when sputtering process is performed. The sputtering process is carried out at vacuum pressure at 235 Pa at applied negative DC voltage at -400 volts and total sputtering time is 6 minutes (continuously). Next, the sample is dipped in concentrated NaOH solution in order to remove dry film in which this process step resulted in patterned of Cu thin film. Finally, the Cu thin film was determined the thickness, morphology, elemental analysis and crystalline structure by various characterization techniques, detailed in next section.

3. Results and discussion

3.1. Thickness and morphology of copper thin film by scanning electron microscope (SEM)

In Figure 3, illustrate the cross sectional SEM image by scanning electron microscope (SEM, model: JEOL JSM-5410LV). The deposition process was performed under vacuum pressure at 235 Pa with -400 volts bias on Cu electrode for 6 minutes depositing time, obtained Cu film with 250 nm in thickness on silicon substrate, resulted in 41.7 nm/min deposition rate. It is seen obviously that the Cu
film was deposit uniformly over the area appeared in Figure 3. For the morphology of Cu film, it is observed that when magnified greater than \( \times 10,000 \) appeared blurred images, therefore the morphology cannot be revealed.

![Cross sectional SEM image of Cu film on Si substrate](image)

**Figure 3.** Cross sectional SEM image of Cu film on Si substrate.

### 3.2. Elemental analysis contained in copper thin film by energy dispersive x-ray spectrometer (EDX)

Elemental analysis of wide scan area of about 20\( \mu \)m\( \times \)30\( \mu \)m (Figure 4 (left), by EDX measurement (equipped on SEM-JEOL JSM-5410LV) observed silicon (Si) atoms for 19.80 at\% and copper (Cu) atoms for 80.20 at\%. It is indicated that the deposited film is a thin copper film, the appearance of Si peak in the EDX spectra point out that the film is thin enough that energetic electron beam able to penetrate through the film reach the substrate surface and then collected signal from silicon substrate.

![EDX scan area in pink rectangular](image1)

**Figure 4.** EDX scan area in pink rectangular (left) and EDX spectra of Cu film on Si substrate (right).

### 3.3. Crystalline structure of the copper thin film by x-ray diffractometer (XRD)

XRD spectra was recorded from X-ray diffractometer (model: Rigaku-MiniFlexII) at \( 2\theta \) through a range of \( 2\theta = 10^\circ \) to \( 20 = 80^\circ \), but \( 2\theta = 60^\circ - 76^\circ \) was illustrated as shown in Figure 5. The dominant peaks were observed at \( 2\theta = 69.3^\circ \) and \( 2\theta = 69.5^\circ \) \([7]\), along with very small peak at \( 2\theta = 61.8^\circ \) \([8]\), were assigned for Si (100) of substrate material. In between \( 2\theta = 20^\circ - 50^\circ \), a broad peak \([9]\) centered at \( 35^\circ \) was detected and it is a characteristic of amorphous structure, as shown in Figure 6.
4. Conclusion
In this work, it is successfully to build a cheaply homemade DC magnetron sputtering system for deposit copper thin film on silicon substrate by assist of polymer mask photolithography. An EDX analysis revealed that the deposited layer on silicon substrate is copper film, as detected Cu atoms. The cross sectional SEM image showed that the Cu film has a thickness of about 250 nm that growth under deposit condition of maintaining voltage at –400 volts at vacuum pressure 235 Pa, in air plasma (which is N₂ based plasma) that the residue gas in vacuum chamber. Morphology of the Cu film

Figure 5. XRD pattern of $2\theta = 60^\circ – 76^\circ$ for Si (100) substrate after deposition of copper thin film.

Figure 6. XRD pattern of $2\theta = 20^\circ – 50^\circ$ for Si (100) substrate after deposition of copper thin film.
cannot be observed by SEM because the limitation of magnification of SEM tool but XRD spectra indicated that the film is amorphous in nature.

Acknowledgement
The author would like to acknowledge the financial support (under grant number MJ.1-59-034) by the office of agricultural research and extension, Maejo University.

References
[1] Meng L J and Dos Santos M P 1996 Thin Solid Films 289 65
[2] Limcharoen A, Pakpum C, Witit-anun N, Chaityakun S and Limsuwan P 2012 AMM. 217-219 712
[3] Pakpum C and Pussadee N 2016 Surf. Coat. Technol. 306 299
[4] Guerra V, Sá P A and Loureiro J 2004 Eur. Phys. J. Appl. Phys. 28(02) 125
[5] Frost D C and McDowell C A 1956 Proc. of the Royal Society of London. Series A. Mathematical and Physical Sciences 236(1205) 278
[6] Tatarova E, Guerra V, Henriques J L and Ferreira 2007 J. Phys.: Conf. Series 71(1) 012010
[7] Thakur M, Isaacson M, Sinsabaugh S L, Wong M S and Biswal S L 2012 J. Power Sources 205 426
[8] Nezamdost J, Zolanvari A, Sadeghi H and Nezamdost J 2013 Middle-East J. Sci. Res. 18(6) 845
[9] Lai T, Yin H and Lind M L 2015 J. Membrane Sci. 489 264