Technology of electroplating copper with low-K material a-C:F for 0.15 um damascene interconnection

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Abstract

. In our work, fluorinated amorphous carbon films (**a-C:F**) was deposited by PECVD. The amorphous carbon films (**a-C:F**) with low dielectric constant (K~2.3), thermal stability (higher than 400°C) and acceptable adhesion to cap-layer such as SiOF was obtained by optimum of content ration between carbon with fluorine and adding few SiH_4 for improvement of adhesion. The etching profile with high aspect ratio and etching selection ration more than 50 (**a-C:F/SiOF**) were obtained by etching gas of N_2+O_2. Furthermore, we demonstrated the technology of electroplating copper in trenches or vias as small as 0.15 µm, 6:1 AR. The wetting agent system was consisted of mainly two molecular weights polyethylene glycols (PEG). The small molecular weight PEG (200) with better diffusion ability for reducing the surface tension and the larger PEG (2000) enhancing grain growth control was proposed for the first time to wet the inner portion of the sub-150 nm damascene feature. The leveling agent system was mainly heterocyclic compound contained N, S atoms offering sufficient activation over-potential and selective inhibition gradient.

Introduction

Dual damascene structure integrating electroplating copper as metal line and low-K material as inter or intra layer for ultra-large-scale integrated (ULSI) chips with sub-0.15um dimensions imposed intense industry-wide efforts on developing novel process, material and integration technology. For the time being, these low-k dielectrics can be classified as organic and inorganic polymers, and these dielectrics can be deposited by either chemical vapor deposition (CVD) or spin-on techniques [1]. For instances, the fluorinated amorphous carbon films (a-C:F)[2-3] were deposited by PECVD, polyimide[1] and HSQ[4] films were deposited by spin coating. In addition, the electrical, chemical, mechanical, and thermal properties are required for these materials and they must be compatible with other processes (e.g., photolithography, etching). Due to the a-C:F film could be deposited by conventional PECVD without changing equipment and the acceptable properties as mentioned, this material became focus of candidates of low-K materials. In our work, fluorinated amorphous carbon films (**a-C:F**) was deposited by PECVD. The basic precursor gas is CH_4, CF_4, C_2F_6, C_4F_8, and dilute silane. .The optimized Amorphous carbon films (**a-C:F**) with low dielectric constant (K~2.3), thermal stability (higher than 400°C), electrically insulating, high mechanical strength, and acceptable adhesion to cap-layer such as SiO_2, SiOF was optimized by ranging content ration between carbon with fluorine and adding few SiH_4 for improvement of adhesion.

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Electroplating process is typically designed for filling trenches and vias by concisely controlled concentrations of additives including levelers. One of the challenges of copper electroplating is the formation of voids in the plated gaps[5] arising from variations in potential and in cupric ion concentration over the plating metal surface[6-7]. Such voids will degrade the conductance and electromigration resistance of copper lines. In addition, the trapped electrolyte can destroy circuits performance and result in a contamination, corrosion, and reliability risk[8].

Basically, the dimension of ULSI applications for the state of art would inherently raise the technical barrier for electroplating copper. Those technical thresholds included such as the electrolyte perfectly diffusing into the quite small space became a more prerequisite condition than anisotropic deposition rate in trenches or vias. The conventional gap filling for lager scale structure is mainly determined by additives of levelers. As the feature size reduced to sub-micron scale smaller than the boundary layer, the transport of cupric ion and the inhibiting additives is dominated by diffusion. Wetting agents are well-known additives for overcoming the capillaceous phenomena generated by the structure of damascene through reducing the surface tension of contour between the electrolyte with opening of trenches or vias. Excepting mass transport, the morphology control of deposited films was another contribution of wetting agent. This is very important for further CMP process. Although that concept is quite intuitive, the applicability would be limited if single wetting agent could not simultaneously exercise perfectly mass transport and control the grain-size growth. We proposed, for the first time; a novel scheme for solving this barrier by moderate combination of wetting agents. This is a new idea for gap-filling study of electroplating copper.

As our approaches, we found that activation over-potential is not the only factor-influencing gap filling performance in deep sub-0.15 μm gaps. By means of those analyses, we have optimized the appropriate amount of additives and achieve the super-filling performance for 0.15 μm vias with aspect ratio 7 by an acid-copper electrolyte with leveler of heterocyclic compounds contained N, S atoms offering sufficient activation over-potential and selective inhibition gradient. Meanwhile, the wetting agent system consisted of mainly two molecular weights polyethylene glycols (PEG) was employed in electrolyte for reducing the surface tension within the small feature with high aspect ratio and achieving grain-size growth control. Concluding unitary effects of additives, there are three indispensable requirements for achieving super-filling property; they are low surface tension of electrolyte, adequate activation over-potential, and sufficient inhibition gradient. If those conditions were present simultaneously during electroplating, then super-filling could be achieved. Our work in this texture may lead to a better understanding of filling chemistry and provide broader process window of solving seed layer coverage, pulse electro-fill, CMP, annealing treatment...etc.

Experimental

The typical process parameter was flow rate C_xF_y/CH_4~10, rf plasma power~200W, process pressure~450mtorr, deposited temperature~300°C. To determine the dielectric constant and leakage current of the a-C:F, MIS (metal-insulator-semiconductor; Al/a-C:F/p^+ Si) capacitor structures were made. The thermal stability and the moisture absorption ability of the films were analyzed by thermal desorption spectroscopy (TDS) and contact angle analyzer.

Our copper electroplating experiments were carried out in Hull Cell. The Hull Cell is a trapezoidal box of non-conducting material with one side at a 37.5-degree angle[9]. The copper anode is laid against the right angle side and the wafer used as cathode is laid against the sloping side. Contact to the electrode was implemented outside of the electrolyte with an alligator clip. Agitation air was introduced into the solution from a compressor. In our experiment, the electrolyte was composed of copper sulfate (30~90 g/l), sulfuric acid (50~200 ml/l), chloride ion (50~100 ppm), wetting agent (20~2000 ppm), and leveling agent (10~200 ppm). All electroplating works were preceded at room temperature. The scanning range was from –400 mV to 800 mV. On the other hand, the cross-section profiles of deposit films were examined by using field emission scanning electron microscope (FESEM). The resistivity of copper deposits was examined by four-point probe measurement.

Characteristics of a-C:F low-K material

The electrical characteristics of a-C:F films are the function of process pressure, content ratio between carbon with fluorine, plasma power etc... As our experimental results, the dielectric constant reduced as increase of F/C, plasma power, process pressure, as shown in Fig.1.a-c. The optimum parameters are in the range of C_xF_y/CH_4~10, RF plasma power~200W, process pressure~450mtorr, deposited temperature~300°C. The total gas flow employed for depositing a-C:F is 300sccm. The typical dielectric constant is $\varepsilon_s = 2.6$, the minimum value is as low as $\varepsilon_s = 2.3$ when the deposition parameters are as process pressure~700mtorr, C_2F_6/CH_4~10 under loss of adhesion quality and thermal stability. The area of aluminum dot for electrical feature measurements is $5.0\times10^{-3}\,\mathrm{cm}^2$. The deposition ratio is $R_d = 1000\,\mathrm{A^o/min}$. If the dielectric constant $\varepsilon_s = 2.5$ of a-C:F films was prepared among various process parameters, the leakage could be controlled about $I_d \approx 5.0\times10^{-8}\,\mathrm{A/cm^2}$ at bias electric field $E_{bias} = 1.5\,\mathrm{MV/cm}$, shown as Fig.2.a-d. Those detailed investigations for the C_xF_y/CH_4 group including the annealing treatment (T=400°C) about the changing of optical index, thickness, contact angle are also implemented. The annealing process was performed in a vacuum furnace filled with N_2, then cooled down to room temperature. The stress for all deposited a-C:F films are below -35Mpa. The electrical characteristics maintained unchanged after 400 °C thermal annealing.

The patterns of damascene structure on wafer could be defined by electron-beam (e-beam) lithography system with resolution below 70nm scale. For integral consideration and reducing the effective capacitor of dielectric layer in damascene feature, the stop layer for dry etching **a-C:F** adopted low-k material fluorinated oxide (SiOF). The novel choice for etching gas in our process is N_2+O_2. Under such recipe, the etching profile and etching selection ration more than 50 **(a-C:F/SiOF)** could be obtained. All wafers were etched in a helicon-wave plasma etching system (ANELVA ILD-4100) with PMT MØRI^{TM} 200 helicon plasma source. RF power of 13.56 MHz was used to generate the plasma and another 13.56 MHz RF power provided the bias to control the ion bombardment energy. The bias power was varied from 0 to 90 W. Etch results were examined by scanning electron microscopy (SEM). Plasma etching was controlled by the three mechanisms: physical bombardment, chemical etching, and chemical passivation. Selective and anisotropic etching can be achieved by a good balance of the above three processes. O_2 and N_2 were used at the total flow rate of 100 sccm. Under RF power~2000W, process presure~5mtorr, bias power~60W, gas flow rate N_2/O_2~80/20, the etching rate for SiOF~180 A°/min and a-C:F~7200 A°/min were obtained. After etching process, the damascene pattern with dimension~150nm was shown as Fig.3.

Electroplating copper for damascene interconnection

In order to overstride threshold of an abruptly increasing gap-filling challenge in sub-150 nm damascene feature, additive chemistries obeying the adsorption-diffusion dynamics must simultaneously provide lower surface tension, sufficient activation over-potential and selective inhibition gradient within the feature. In general, adding wetting agent is capable of lowing surface tension of the feature. Improving sufficient activation over-potential and selective inhibition gradient within the feature would be implemented by adding effective levelers to plating baths.

Through reducing surface tension of the trenches or vias, cupric ions and additives in the electrolyte could easily transport into the deep-gap and copper could be deposited within the feature. Main point of view of the wetting agent formulation is that the lager molecular weight PEG (2000) with higher surface tension wets the outer region or the shoulder of the feature. The smaller molecular weight PEG (200) with lower surface tension wets the sidewall or bottom of the feature. Although single wetting agent PEG (200) will improve the wetting effect in small feature with scale below several hundreds nm, but rough deposited copper surface was the appendant due to its lower inhibited copper deposition current. Observing Fig. 4-a and 5-a, single wetting agent PEG (2000) just carried the electrolyte diffused into outer portion of via and produced a brighter surface due to PEG (2000) with more hydrophobic groups. Those chemical groups act as a grain refiner. While the grain refinement of electrolyte with wetting agents PEG would not increase apparently the resisivity of copper films, the major attributors on affecting the resisivity of copper films were levelers. For the case of PEG (200), inner portion of AR 5:1, 0.18 μm via could be wetted but deposited copper surface was rough in macroscopic standard than the case of PEG (2000) observed as Fig. 4-b and 5-b. Observing Fig. 4-b, the existing defects or voids were due to the PEG (2000) and levelers were not included in electrolyte. In order to enforce the electrolyte to be pulled into sub-150 nm trenches/vias by capillarity and improve the quality of electroplating copper, we add wetting agents that contain two molecular weights of PEG to the plating bath. Evidence for wetting agents consisted of two molecular PEG employed to fill 0.15 μm via with high aspect ratio and beyond was shown in Fig. 6 (b). Concluding above discussions, it was understood as that wetting or mass transport phenomena were consistent with the threshold of a surface tension. Above this specified value, a liquid would no longer wet small gap with high aspect ratio. This limitation could be overcome by the electrolyte with low molecular weight carriers transporting cupric ions and leveler into deep gap. The low surface tension electrolyte combining stronger growth inhibition effect provided both mass transport and grain growth control simultaneously.

Due to the structure of our interested trenches/vias for ULSI applications is very asymmetrical, the filled copper with void or seam would be obtained if inherent isotropic or weak anistropic deposition rate were not changed. Copper electroplating for damascene interconnection by adding leveling agents in the electrolyte to enhance the filling capability has been investigated[10-11]. The stronger bottom-up filling capability is a key issue for deep sub-micro and high aspect ratio damascene structure.

In order to distinguish the efficiency of different leveling agents in the deep gap more easier, we adopted the larger dimension patterns (about 1 μm, AR: 1) and calculated the anisotropic deposition ratio $\Delta y/\Delta x$ of partially filled trench profile to quantify the leveling power of additives. Through measuring transient cross-section SEM profiles of partially deposited trenches/vias, the deposition rates of two coordinate axes X, Y were calculated for horizontal and perpendicular directions referencing to side-wall and bottom of gap respectively. In Fig. 6 (a), the patterned wafer before electroplating was composed of a 30-nm thick CVD-Ti/TiN layer as the diffusion barrier and a 200-nm thick IMP-Cu film as the seed layer. In gap-filling experiment, the electrolyte was composed of copper sulfate (30 g/l), sulfuric acid (275 g/l), chloride ion (100 ppm), wetting agent (20~2000 ppm), and leveling agent (10~200 ppm). In Fig. 6 (b), we could observe that the super-filling effect was achieved in vias below 150 nm by using thiazole derivatives as the leveler. The common characteristics of these additives performed as levelers through incorporation of CuS in plated copper films. Inhibition of the plating rate and increasing the number of nucleation generated small-grained films. Concentration gradient of an inhibition additive such as 2-aminobenzothiazole could lead to higher plating rates near the bottoms of trenches/vias than neighborhood of topper of interfacial boundary between electrolyte with copper seed layer. Even that, the leveler in deep sub-micron trenches/vias were also controlled by adsorption-diffusion excepting consumption effects as previously considering. Diffusion behavior on leveling effect was assumed that additive flux is diffusion limited and that the inhibition extent of plating rate can be related to additive concentration gradient. Based on the diffusion of leveler, the inhibition of topper of gap was stronger by more concentration distribution of additives. We could conclude that the additives employed as levelers must provide moderate inhibition effects and gradient inhibition ability, meanwhile; those dynamics were under control of interaction of consumption, adsorption, and diffusion.

Conclusions

The optimized Amorphous carbon films (**a-C:F**) with acceptable adhesion to cap-layer such as SiO_2, SiOF was optimized by ranging content ration between carbon with fluorine and adding few SiH_4 for improvement of adhesion. The etching gas in our process is N_2+O_2. Under such recipe, the perfect etching profile and etching selection ration more than 50 (**a-C:F/SiOF**) was demonstrated. Technology of electroplating copper in trenches or vias as small as 0.15 μm, 6:1 AR has been developed by typical acid-copper electrolyte with complex additives. Transport of cupric ions and levelers were enhanced by complex wetting agents that consisted of mainly two molecular weights polyethylene glycols (PEG). Among the functional group chemical achieving super-filling, 2-aminobenzothiazole could provide the very high filling ability and quite low resistance (R = 2.5 μΩ-cm) as-deposit.

Acknowledgments

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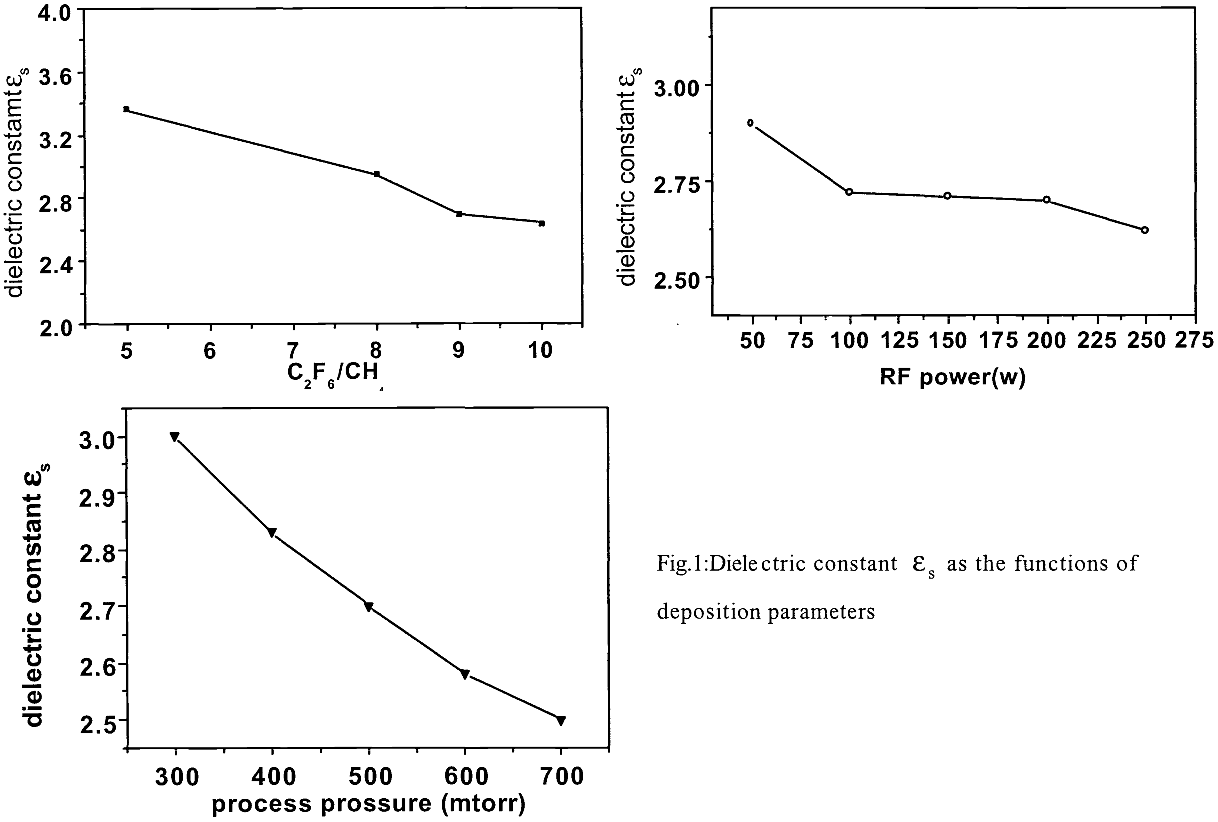


Fig.1:Dielectric constant ε_s as the functions of deposition parameters

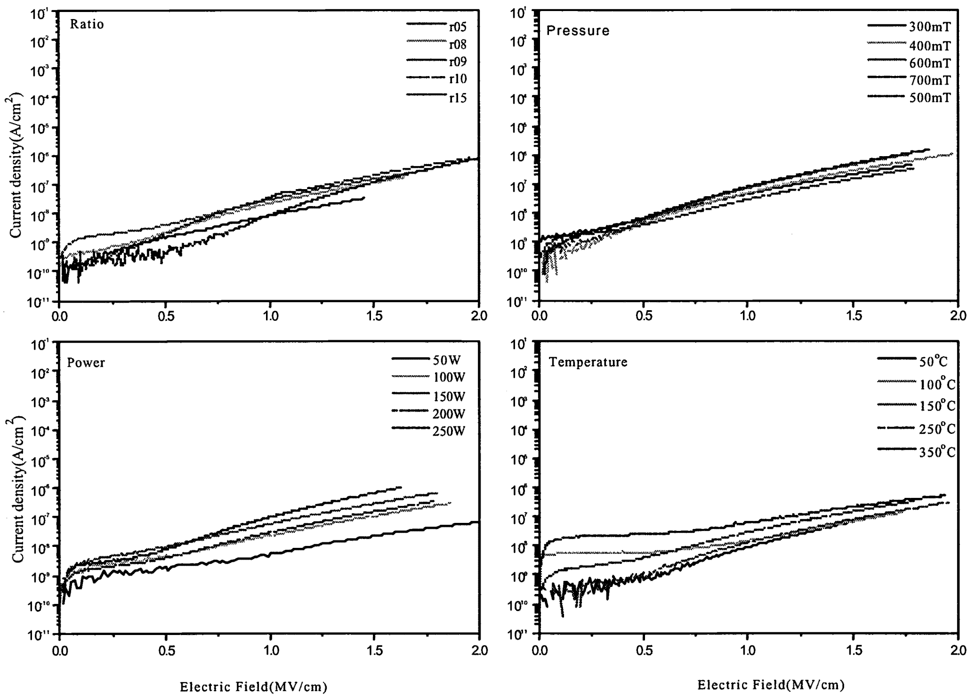


Fig. 2: The leakage currents as the functions of deposition parameters

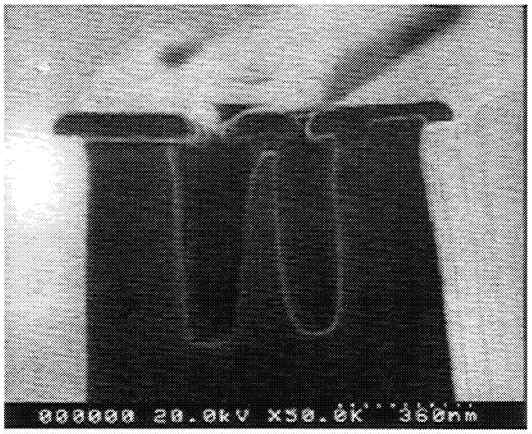
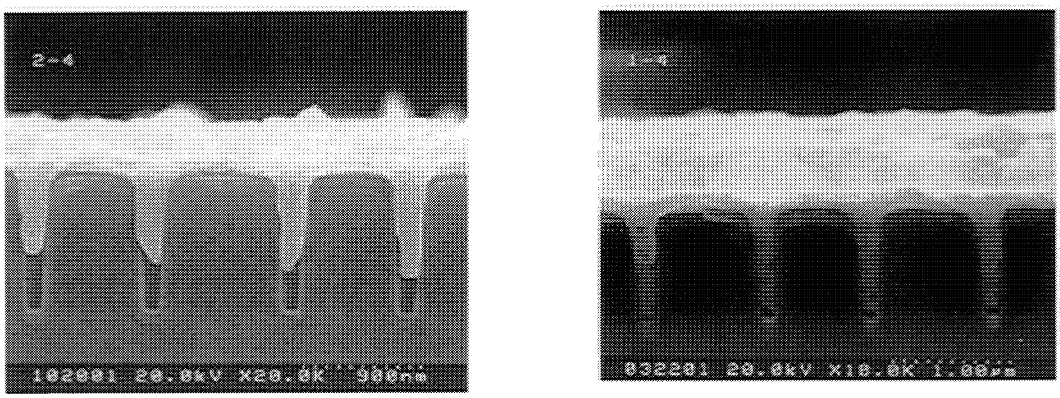
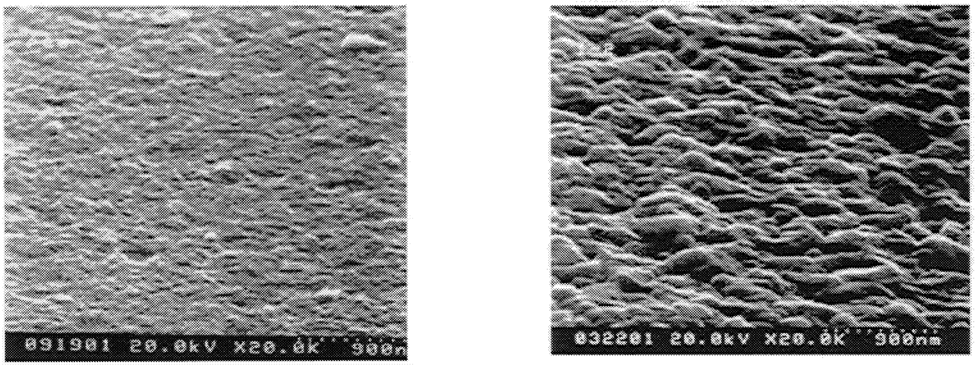


Fig.3:After etching process, the damascene pattern with dimension~150nm.



(a) PEG2000 (b) PEG200

Fig. 4: (a) the filling profile of AR 5:1, 0.18 μm via was electroplated by adding PEG (2000) as wetting agent, (b) the filling profile of AR 5:1, 0.18 μm via was electroplated by adding PEG (200) as wetting agent.



(a) (b)

Fig. 5: (a) the surface morphology of copper films by adding PEG (2000) as wetting agent, (b) the surface morphology of copper films by adding PEG (200) as wetting agent.

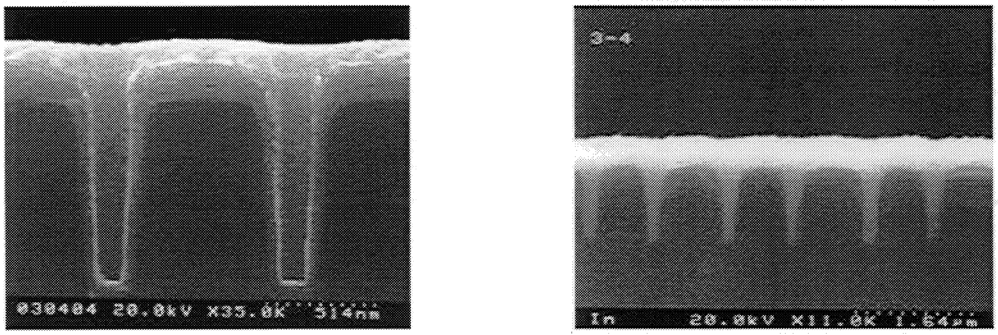


Fig. 6: (a) the AR 6:1, 0.15 μm patterned wafer before copper electroplating

(b) the bottom-up filling effect was achieved in AR 6:1, 0.15 μm via by using 2-aminobenzothiazole as the leveler.