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Micro-scale modification of diamond-like carbon and copper electroplating by scanning probe field emission current method

Shigehiro Hayashi [a,*], Yuki Antoku [a], Younggun Han [b], Woon Choi [a], Hajime Tomokage [a]

[a] *Department of Electronics Engineering and Computer Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan*

[b] *Fukuoka Industry, Science & Technology Foundation, 1-1-1 Tenjin, Chuo-ku, Fukuoka 810-0001, Japan*

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ABSTRACT

Micro-scale modification of nitrogen-doped diamond-like carbon (DLC) is performed by applying an electric field between a tungsten tip and DLC film surface in vacuum using the scanning probe field emission current (SPFEC) method. The dc voltage ranging from −700 V to −3000 V is applied to the tip. Then, electroplating of Cu is performed on the DLC film surface in $CuCl_2$ solution by a three electrode-cell. The cathodic polarization curves indicate that the start potential of Cu on modified DLC film is shifted to a lower value than that of Cu on an as-grown DLC film. Cu deposits selectively on the DLC surface modified by an electric field. With this technique, the micro-scale patterning of Cu can be achieved by electroplating without a lithographic process.

1. Introduction

Fabricationof micro/nano-scale structures on silicon wafer and print circuit boards (PCB) is one of the key technologies to produce electronic devices. The interconnection of advanced integratedcircuits (ICs) are made by Cu because of its lower resistivity, higher allowed current density and better reliability than aluminum alloys. The copper interconnection for ICs has been fabricated with Cu electroplating followed by chemical-mechanical-polishing (CMP). The conducting patterns

* Corresponding author. Tel.: +81 92 871 6631.
E-mail address: td076501@cis.fukuoka-u.ac.jp (S. Hayashi).

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on PCBs made by Cu have mainly employed a subtract process and an additive process. For both processes, lithography with masks is always used for electroplating. Also, the removal process of deposited metals with resists is basically required through dry/wet etching in order to fabricate metal patterning. Although the maskless process could reduce the cost of metallization, the patterning of electroplated Cu requires photolithography.

Recently, electrochemical approaches have been utilized in the electronics industry because of simplicity and low cost. The another advantage is that they can deposit selectively at the sites where the electron transfers to metal ions. A number of attempts have been reported to utilize electrochemical approaches for the fabrication of micro/nano-structures without a photolithographic process [1–4]. Laser–induced metallization of various substrates with micro/nano-scale resolution is well known [3,4]. For porous silicon, Ogata et al. [3] demonstrated that Cu was selectively electroplated only at the illuminated part of porous silicon by utilizing the rectifying properties of the Schottky barrier formed at p-type semiconductor/solution interface [3]. Also, by modifying the local region at the surface, it is expected to achieve a non-photolithographic process by selective metal deposition using electrochemical processes. However, there has been no report on an electrochemical process for non-semiconductor materials.

Diamond-like carbon (DLC) films, on the other hand, have an amorphous structure composed of sp^2 bonds and sp^3 bonds. DLC films have been studied because of their unique properties such as chemical stability, optical transparent, mechanical property, low electron affinity and wide potential window for water stability [5] depending on sp^2/sp^3 bond ratio, doping element and doping level. Some researchers have suggested that DLC surface could be modified by applying a local electric field from the DLC surface to a probe [6,7]. In order to perform modifications, a series of voltage pulses were applied between the sample and the probe [6–9]. Mercer et al. [8] demonstrated that spatially resolved electron energy loss spectroscopy measurements had indicated an increase in the ratio of threefold-coordinated C to fourfold-coordinated C within the area treated by a scanning tunneling microscope (STM) [8]. However, it is difficult to perform the modification of conducting patterns on IC and PCB by STM. Furthermore, the surface modification by applying an electric field between the DLC surface (as a cathode) and tungsten tip (as an anode) sometimes creates serious damage [10].

In this paper, we propose a way to electroplate Cu selectively on DLC films without any mask or lithographic process. After applying the electric field to the DLC film by a scanning probe field emission current (SPFEC) method, Cu deposits selectively on the DLC surface modified by SPFEC. Since no lithographic process is needed for Cu electroplating, this method is promising for fabricating fine patterns in ICs and PCBs.

2. Experimental procedures

An N-type Si (100) wafer was used as a substrate in this work. The wafer was cleaned in acetone and ethanol, de-ionized water for 5 min into ultrasonic bath, respectively. DLC films were grown on an n-Si surface in a gas mixture of CH_4 and N_2 atmospheres by radio frequency plasma-enhanced chemical vapor deposition (RF PE-CVD). The total gas pressure was 10 m Torr with nitrogen pressure of 1 m Torr. DLC films were deposited approximately 700 nm in thickness with the constant negative self-bias voltage of −900 V. Then, an aluminum electrode for electroplating was evaporated on to the rear side of the n-Si substrate.

Fig. 1 shows the schematic diagram of SPFEC apparatus. The dc voltage ranging from −700 V to −3000 V is applied to the probe in high vacuum lower than 3×10^{-6} Pa. A protective resistance (R_P) is connected between the probe and an ampere meter. The X and Y-axes of the sample stage move with a resolution of 1 μm and the Z-axis with resolution of 0.1 μm. The Z-axis of probe position is calibrated by using a resistance measurement to contact the corners of a modification area on the sample, then the probe height above the sample is determined by moving the probe away from the sample. The surface modification in the micro-scale region on the DLC films was performed by moving the stage for a fixed probe height above the sample under a dc voltage condition. The electric field process was controlled and monitoring on the computer system by GPIB.