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Short Paper

LOW TEMPERATURE DIRECT ELECTROLESS NICKEL PLATING ON SILICON WAFER

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ABSTRACT

In the study of electroless nickel (EN) plating on n-type (100) silicon wafers, a relatively low-temperature alkaline plating process is developed. Further experiments show that simple ethanol pretreatment of the substrate is practicable for obtaining an EN layer with a good adhesion strength of about 9.8 to 14.7 MPa. Both sodium tungstate and sodium fluoride can be used to decrease the threshold plating temperature from near 80°C to 65°C. The phosphorous content of the as-plated layer is slightly higher than 7 wt.%.

Key Words: electroless nickel, silicon wafer, ethanol pretreatment, adhesion strength.

I. INTRODUCTION

Electroless nickel (EN) plating is widely used in microelectromechnical systems (MEMS) and the semiconductor industry. Unlike the electroplated nickel layer, EN deposits have uniform thickness on any area exposed to the plating solution. As long as the substrate has been well pretreated, the electroless chemical reduction process can take place, whether on metallic or non-metallic substrates. Because there is no limit to the substrates, and no build-up at sharp corners or edges, we can take advantage of this process with some semi conductive substrates such as silicon wafers.

In 1957, Sullivan and Eigler first applied EN plating to make ohmic contacts on silicon (Sullivan and Eigler, 1957). The plating solution they used contained NH_4^+, and the plating temperature was relatively high (90~100°C). NH_4^+ is volatile under high plating temperature and thus harmful. Besides the safety considerations, there also existed thermal stress due to the temperature gradient. Ohring (Ohring, 1992) proposed a formula to estimate the thermal stress for EN layer: $\sigma t = \frac{\Delta\alpha \times \Delta T \times E_f}{1 - v_f}$, where $\Delta\alpha$ is the thermal expansion coefficient difference between silicon wafer and general electroless Ni-P layer. This formula shows that the thermal stress is proportional to ΔT, which is equal to the difference between the plating and ambient temperature. The development of low-temperature EN plating is therefore also helpful in reducing the thermal stress and maintains the stability of the as-plated EN layer. Generally speaking, low-temperature EN plating can be accomplished by choosing certain appropriate complexing agents such as pyrophosphate or citrate to decrease the activation energy of the reduction action (John *et al.*, 1982). Chen et al. used low-carbon steel and brass sheet as substrates and found that sodium tungstate decreased the threshold temperature of EN plating remarkably (Chen and Chen, 1997). With 44 g/L sodium tungstate in the alkaline plating bath, the threshold temperature can be lowered to 38°C. Furthermore, the phosphorous content in the EN layer is low.

The electroless plating solution is mainly composed of a nickel source, a reducing agent, and a complexing agent. Nickel ions are often provided by nickel sulfate. The reducing agent can be selected as sodium hypophosphite or sodium borohydride, where the as-plated layer contains phosphorous or boron, respectively. The phosphorous or boron content is

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critical in determining the crystallinity of the EN layer. In an Ni-P deposited layer, for example, when phosphorous content(wt.%) is above 7%, the EN layer is amorphous (Spencer, 1974), has no grain boundary, and serves as a good diffusion barrier layer to prevent interdiffusion between the Al or Cu layer and solder bump in flip chip packaging.

Although the reducing agent plays an important role in the reduction reaction, Takano et al. (Takano *et. al.*, 1999; Takano *et. al.*, 2000) found that EN plating on silicon wafers is still practicable even without the reducing agent. From their viewpoint, when Si oxidizes to SiO_2, the electron released can cause the nickel ion to reduce to nickel. As a result, the extra electron source is unnecessary.

There are still some shortcomings in EN plating on silicon reported in the literature (Bhansali *et al.*, 1997). First, the substrate should be exposed to at least four complicated liquid processing and rinsing steps before plating. Secondly, the adhesion strength of electroless plated structures is relatively poor because the bonding is not atomic but mechanical in nature. The substrate should be lightly etched by a certain reagent (generally HF) to anchor the nickel films mechanically. Thirdly, there is no direct control of the plating solution. Many factors, such as temperature and additives, will influence the plating quality.

In the traditional viewpoint, a clean and catalytic surface without oxide layers after pretreatment is necessary (Valova, 1994). Improper pretreatment can create passive spots that will not initiate electroless plating and result in non-uniform deposition, causing porosity. To start the EN reaction on the silicon wafer, the wafer surface need to be sensitized by $SnCl_2$ and activated by $PdCl_2$. In 1961, Shipley first developed one patent for an EN process which mixes $SnCl_2$ and $PdCl_2$ in HCl (Shipley, 1961).

Takano et al. thought Ni^{2+} approached the hydrophilic surface more easily than the hydrophobic surface (Takano *et. al.*, 2000). But if we use HF to eliminate the original oxidized layer, the surface will be covered by hydrogen existing as dihydride phase and become hydrophobic (Sebastiao *et. al.*, 1997), which is undesirable for the EN plating reaction. Furthermore, they dramatically found that the adhesion strength was effectively improved by a simple ethanol pretreatment. The effort of this paper has been concerned with the development of a convenient EN plating process on n-type (100) silicon wafers under relatively low plating temperature through modifying Takano's pretreatment procedure.

II. EXPERIMENTAL

The substrates used were n-type (100) P dopant silicon wafers with a manufactured polished surface. The wafer was cleaned by the RCA process and then cut 1nto 0.5×1 cm^2 pieces by a diamond knife. Directly prior to plating, all pieces were totally immersed in ethanol for 30 minutes, but without traditional activation and sensitization steps.

The composition of the plating solution is

$NiSO_4 \cdot 6H_2O$	40 g/L
$Na_3C_6H_5O_7 \cdot 2H_2O$	60 g/L
$NaH_2PO_2 \cdot H_2O$	0~40 g/L
$Pb(CH_3COO)_2 \cdot 2H_2O$	1.5 ppm
$C_{12}H_{25}O_4SNa$	1.5 ppm
Saccharin	8 g/L

In this composition, $Pb(CH_3COO)_2 \cdot 2H_2O$ acted as a stabilizer to control the concentration of free Ni^{2+}, and $C_{12}H_{25}O_4SNa$ acted as surfactant to help hydrogen bubbles escape away from the wafer more easily. To control the operating conditions, NH_4OH has been employed to adjust the PH value of the plating solution. In all experiments, we compounded 100 ml fresh plating solution that included 32 ml NH_4OH. The original load of this plating solution was 5 cm^2/dm^3. The plating bath was stirred and heated moderately. For the investigation of the effect of plating conditions on the plating rate of nickel layers, the plating temperature was carefully maintained at 80°C. The average thickness of the EN layer was measured via a surface profiler (Alpha-Step 500). From the measured average thickness and the total plating duration, the plating rate can be calculated.

The threshold temperature of plating is defined as the temperature at which the plating reduction reaction of nickel ions begins. This reaction can be indicated by the onset of hydrogen bubbles found on the surface of the silicon wafer (Chen and Chen, 1997). All plating reactions, if proceeding successfully, were sustained for one hour. The phosphorous content of EN layer can be analyzed by Energy Dispersive Spectrometry (EDX). To measure the adhesion strength between the as-plated EN layer and the silicon wafer, an adhesion tester as shown in Fig.1 was used. After adhesion testing, the fractography of the Si/Ni-P specimens was observed by scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

When the silicon wafer is subjected to the ethanol pretreatment, an EN layer can be successfully

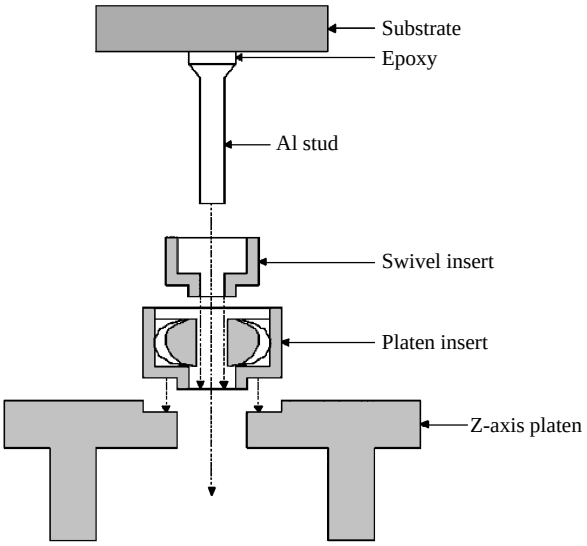

Fig. 1 Equipment for measuring the adhesion strength of EN plating layer on Si wafer

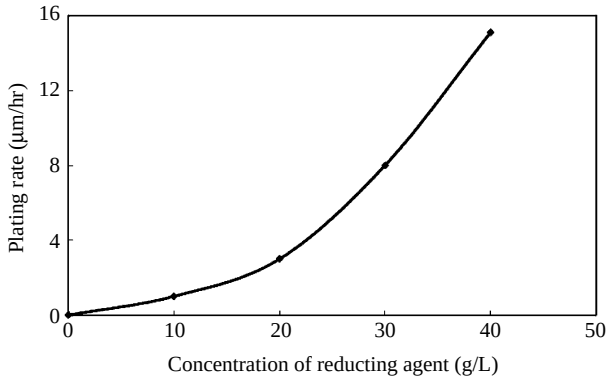

Fig. 2 The relation between the amount of the reducing agent and the plating rate of nickel layers

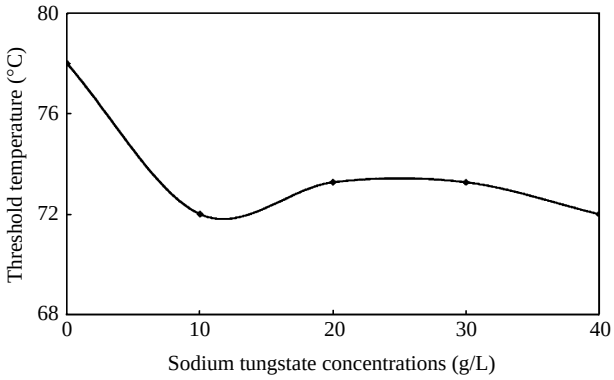

Fig. 3 The effect of sodium tungstate concentrations on the threshold temperature for EN plating

plated on its polished face. In comparison with the traditional sensitization pretreatment method involving the use of an activation agent composed of heavy metal such as palladium to produce active sites, the operating cost is remarkably reduced. It is known that the O-H bond in ethanol tends to produce a hydrophilic surface. Glycerol, which contains three O-H bonds, has been used as the pretreatment agent. However, the following EN plating process leads to a result no better than those using the ethanol pretreatment process.

Because EN plating is an autocatalytic reaction, the nickel plating layer will continuously deposit at the bath temperature when the necessary activation energy has been overcome. Fig. 2 shows the relation between the amount of the reducing agent and the plating rate of nickel layers. With increases of the concentration of the reducing agent, the plating rate becomes higher. But no plating reaction occurs when there is no reducing agent. This result is different from that of Takano et al. It can be seen in Fig. 2 that the highest plating rate is about 15.1 μm/hr, which is commensurate with Iwasa's results for n-type silicon wafers (Iwasa *et al*., 1968). Following the above results, 40 g/L $NaH_2PO_2 \cdot H_2O$ was selected as the optimum reducing agent concentration for the plating solution to develop the low-temperature plating process.

Figure 3 shows the effect of the addition of sodium tungstate on the threshold temperature for nickel plating. There was indeed an obvious decrease of the threshold temperature from 78°C to 72°C after 10 g/L sodium tungstate was added to the plating bath. With further increases of the concentration of the sodium tungstate in solution, the threshold temperature remained almost constant.

Chen *et al*. reported that NaF can be added to the solution to obtain a low-temperature plating effect (Chen and Chen, 1997). It has been shown in our study that the threshold temperature decreased to 65°C when 6 g/L NaF was added to the plating solution. However, increasing the NaF content to 12 g/L caused the plating solution to become very unstable and bubble severely. As a result, the solution containing 10 g/L sodium tungstate and 6 g/L NaF has been considered as the optimal composition for the low-temperature EN plating. From the EDX analysis, the phosphorous content was slightly higher than 7 wt.%. Furthermore, although the plating solution was composed of sodium tungstate, no trace of tungsten has been found in the EN layer.

The adhesion strengths of the Si/Ni-P specimens as measured were about 9.8 to 14.7 MPa. Fig. 4 shows the fractography of an adhesion tested specimen, which has been plated under the above optimum plating conditions. It can be seen that the breaking path penetrates deeply into the Si substrate. The result

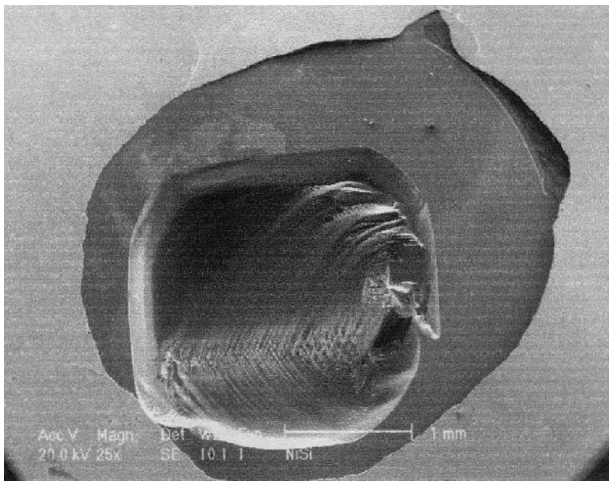

Fig. 4 The fractography of Si/Ni-P specimen produced under the optimal plating condition after adhesion strength test

indicates that the EN plating nickel layer has been tightly bonded with the Si wafer.

IV. CONCLUSIONS

For EN plating on the n-type (100) silicon surface, it has been shown that the ethanol pretreatment is more convenient and advantageous than the traditional roughening, sensitizing, and activation processes. Using the solution containing 40 g/L $NiSO_4$, 40 g/L NaH_2PO_2, 60 g/L $Na_3C_6H_5O_7$, 8 g/L saccharin, 1.5 ppm $Pb(CH_3COO)_2 \cdot 2H_2O$, 1.5 ppm $C_{12}H_{25}O_4SNa$, and 32 ml/L NH_4OH, an electroless Ni-P layer can be plated at 80°C with a plating rate of about 15 μm/hr. When 10 g/L sodium tungstate was added to the plating bath, the threshold temperature decreased to 72°C. With an extra addition of 6 g/L NaF, the threshold temperature was further reduced to 65°C. The adhesion strengths of the electroless plating Ni-P layers on Si wafers under the optimal plating condition were about 9.8 to 14.7 MPa. The fractography of the Si/Ni-P specimens after adhesion tests confirms the sound bonding between the Ni-P layer and the Si wafer.

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