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Invited Paper

Low temperature Cu—Cu thermo-compression bonding with temporary passivation of self-assembled monolayer and its bond strength enhancement

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ABSTRACT

Self-assembled monolayer (SAM) of alkane-thiol is formed on copper (Cu) thin layer coated on silicon (Si) wafer with the aim to protect the surface against excessive oxidation during storage in the room ambient. After 3 days of storage, the temporary SAM layer is desorbed with *in situ* anneal in inert ambient to uncover the clean Cu surface. A pair of wafers is bonded at 250 °C. Clear evidences of in-plane and out-of-plane Cu grain growth are observed resulting in a wiggling bonding interface. This gives rise to enhancement in shear strength in the bonded Cu—Cu layer.

1. Introduction

Three-dimensional integrated circuits (3-D ICs), in the form of a stack of several vertically bonded and interconnected thinned IC chips, offer benefits in terms of performance, form factor, density, heterogeneous integration, and power consumption [1,2]. Inter-chip vertical connection is usually accomplished by through-silicon via (TSV). The thinned IC layers can be bonded by way of Cu—Cu bonding [3] and a four-layer stack has been conceptually demonstrated previously [4]. 3-D integration of ICs using bump-less Cu—Cu bonding is an attractive option because one can use the bonding medium as an electrical bond to establish a conductive path between the active layers and as a mechanical bond to hold the active layers together reliably. It is also possible to form hybrid bond that consists of Cu and dielectric such as benzocyclobutne (BCB) [5] and oxide [6]. Cu—Cu bond is desired compared to solder-based connection because: (1) Cu—Cu bond is more scalable and ultra-fine pitch can be achieved; (2) Cu—Cu bond has better electrical, mechanical, and thermal properties as no inter-metallic compound is formed; and (3) Cu has much better electro-migration resistance and can withstand higher current density in future nodes.

Cu—Cu bonding has been demonstrated using thermo-compression bonding via parallel application of heat and pressure [7,8]. The bonding mechanism is based on inter-diffusion of Cu atoms and grain growth across the bonding interface. Since Cu surface oxidizes readily in ambient air, an oxide barrier is formed and it hinders successful bonding at low temperature. However, there is strong motivation to accomplish Cu—Cu bonding at low temperature for thermal budget consideration, lower thermal–mechanical stress, and alignment control. One method is to remove the surface contaminant with energetic ions and bond the Cu surfaces in ultra-high vacuum (UHV) ambient but this surface activated bonding (SAB) method has several constraints during manufacturing [9]. Oxide reduction with forming gas anneal [10] has been demonstrated, but surface contamination of particles from wafer handling can still remain a challenge. Oxide removal with wet cleaning such as acetic acid [8] has been used with some success. However, acetic acid is also found to etch the Cu layer hence making process control challenging. All these methods [8–10] provide a clear direction that oxide free Cu surface, preferably prepared by non-vacuum and non-corrosive means, is promising to accomplish thermo-compression bonding at low temperature.

In this work, we propose to use self-assembled monolayer (SAM) of alkane-thiol [11] to passivate the clean Cu surface immediately after metallization. Alkane-thiol has previously been used by Maex et al. to passivate Cu bond pad surface and resulted in significant improvement of the non-stick percentage during wire bonding [12,13]. However, the application of alkane-thiol as surface passivation layer to enhance Cu thermo-compression bonding (particularly on bump-less Cu thin layer) at low temperature (<300 °C) is not widely studied yet [14]. In this letter, the role of SAM in protecting the Cu surface against excessive oxidation is discussed and improvement in the final mechanical shear strength of the bonded Cu—Cu layer is reported.

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2. Experimental

Fig. 1 shows schematic of the process flow used in this experiment. All wafers used in this work are *p*-type 150 mm Si-(1 0 0) test wafers with resistivity in the range of 3–50 Ω cm. Silicon wafers are first cleaned with standard RCA clean prior to thermal oxidation to form 500 nm thick of silicon dioxide. Piranha clean (H_2O_2:H_2SO_4 = 1:1) is performed next for pre-metal cleaning. Metal deposition is done consecutively in a sputtering chamber for ~75 nm of Ta (as Cu diffusion barrier) and ~100 nm of Cu. As-sputtered Cu wafers are immersed into the solution of 1-hexanethiol (95%, Sigma–Aldrich), denoted as C6 in the subsequent text. C6 is dissolved in ethanol to a concentration of 1 mM and stored in nitrogen-purged dry box for a specified time interval. Cu wafers are then taken out and rinsed with ethanol to remove the unabsorbed C6 molecules and blown dry under nitrogen gas. The wafers are then used for various experiments as described next. Various analyses are then performed to characterize the modification of the Cu surface properties.

3. Results and discussion

The alkane-thiol used in this work is 1-hexanethiol [CH_3—$(CH_2)_4$—CH_2—SH] and it consists of a methylene (CH_2) chain backbone with a thiol (-SH) head group at one end. At the other end of the carbon chain, there is a tail group of methyl (—CH_3) which is hydrophobic. The thiol group shows strong affinity for face-centered cubic (FCC) metals such as Cu and form S—Cu bond with the Cu surface. The self-assembled monolayer (SAM) is formed by the adsorption of the carbon chains onto the surface through the development of bonds between the S head groups and the surface metal atoms. The molecules then orient themselves away from the surface so that the methylene chains are parallel to each other and tilted in order to maximize the van der Waals interactions between them, thereby leaving the tail groups exposed at the surface. This results in an orderly and densely packed molecule monolayer on the Cu surface. The aim in this work is to use SAM as a temporary passivation film to slow down oxygen diffusion and reaction with the Cu surface. This preserves the cleanliness of the surface to assist in bonding as surface oxide is known to hinder bonding particularly at low temperature. SAM layer can be readily desorbed *in situ* prior to bonding in a controlled ambient hence resulting in clean Cu surfaces to assist in Cu inter-diffusion and hence to improve the final bonding quality. SAM is an attractive choice as it is harmless to the back-end processes, easy to handle, low cost, "greener" compared with flux or other surface finishes [15] and it has been shown to exhibit superior passivation property compared to well known Cu passivator such as benzotriazole (BTA) [13,16] that is used to passivate Cu after chemical mechanical polishing (CMP).

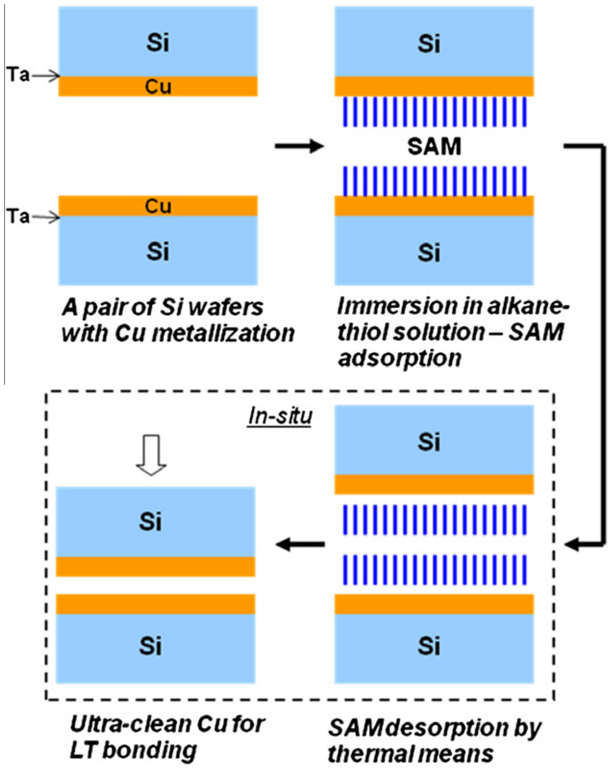

Fig. 1. The application of self-assembled monolayer (SAM) as a passivation layer on Cu surface for bonding enhancement at lower temperature. The process flow includes post-metallization absorbtion and pre-bonding *in situ* desorption to provide clean Cu surfaces for bonding.

The adsorption property of C6 on the Cu surface during immersion can be monitored from water contact angle (CA) measurement by a static sessile drop method using a Surftens^{HL} (OEG) tool. The surface wettability, as determined by the CA profile captured by goniometer, can provide an indication of the surface modification due to the presence of C6 SAM. Freshly sputtered Cu shows a CA value of 22.3° as previously reported [14]. As summarized in Fig. 2, this value increases very rapidly to 93.4° after 2 h of immersion in the C6 solution. The Cu surface turns from hydrophilic to hydrophobic because C6 molecules bind to the Cu surface via the thiol (—SH) groups and form a SAM layer. The methyl (—CH_3) groups modify the surface to be more hydrophobic.

Since the SAM layer is used as a temporary protective film, it must be desorbed to uncover the clean Cu surface in a controlled environment before wafer-to-wafer contact and bonding. The SAM passivation layer needs to be completely desorbed to prevent out-gassing as previously observed [17]. Desorption can be accomplished by annealing the SAM passivated wafers in an inert ambient at 250 °C for 10 min. In Fig. 2, CA value recovers to 28.2 °C and 34.2 °C for annealing in vacuum (~1e−4 mBar) and N_2 respectively. The discrepancy between the CA values with that of fresh Cu (*i.e.,* 22.3°) is related to residual oxide on Cu surface. Surface oxidation is known to give rise to the CA value [17]. Since there is a brief delay between Cu sputtering and immersion in alkanethiol solution, Cu surface gets oxidized slightly prior to passivation. Higher CA value with N_2 annealing is believed to be related to purity (<100%) of the N_2 gas used in the experiment.

After 2 h of immersion, a pair of C6-treated wafers is kept in clean room ambient for 3 days along with a pair of control Cu wa-

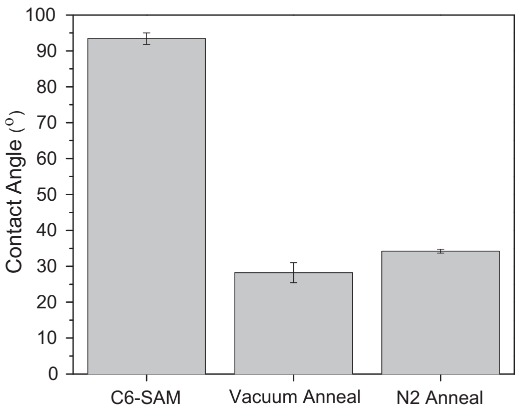

Fig. 2. Cu surface modification due to SAM formation (immersion in C6 solution for 2 h), and thermal desorption in inert ambient (vacuum and N_2) at 250 °C for 10 min.