



Effect of surface oxide on the melting behavior of lead-free solder nanowires and nanorods

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ABSTRACT

Lead-free nanosolders have shown promise in nanowire and nanoelectronics assembly. Among various important parameters, melting is the most fundamental property affecting the assembly process. Here we report that the melting behavior of tin and tin/silver nanowires and nanorods can be significantly affected by the surface oxide of nanosolders. By controlling the nanosolder reflow atmosphere using a flux, the surface oxide of the nanowires/nanorods can be effectively removed and complete nanosolder melting can be achieved. The complete melting of the nanosolders leads to the formation of nanoscale to microscale spherical solder balls, followed by Ostwald ripening phenomenon. The contact angle of the microscale solder balls formed on Si substrate was measured by direct electron microscopic imaging. These results provide new insights into micro- and nanoscale phase transition and liquid droplet coalescence from nanowires/nanorods to spheroids, and are relevant to nanoscale assembly and smaller ball grid array formation.

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1. Introduction

One-dimensional nanostructures, especially nanowires, have received substantial interest in recent years due to their outstanding electrical, optical, magnetic and biological properties. However, there are still several technical obstacles against fully use of the unique properties of nanowires, which hinder the fast growth and adoption of nanowire applications. Among the important issues, a common problem in nanowire assembly and integration is unreliable interconnection between nanowires and nanowires or between assembled nanowires and electrodes/contact pads; thus, the joining of nanowires has become a critical issue for nanoelectronics assembly and packaging. Various joining processes such as welding, soldering and mechanical bonding have been proposed for the formation of nanowire interconnects [1,2]. Among various techniques proposed in the past several years, nanosoldering is a unique technique gaining increasing interest. Solder materials have been widely used in electronics assembly and board level packaging. Due to the environmental and health concern of lead, the classical tin/lead (Sn/Pb) solders are being phased out and lead-free solders in the form of binary, ternary or quaternary alloys are being extensively studied as replacements. Nanowires

that contain nanosolders can be used to bond various nanocomponents or integrated surfaces. Besides the intensive research on the synthesis and fabrication of nanostructured solders, including tin/silver, tin/copper and tin/silver/copper (SAC), the thermal and electrical properties of Pb-free nanosolders in both nanoparticles and nanowires are being studied and their applications are being explored [3–5].

Reflow soldering is the most common method of chip level packaging and joining electrical components to circuit board by heating the solders and adjoining surface. There are many parameters to evaluate the property and quality of solders during the reflow. Wettability is one of those important parameters which can be experimentally assessed by measuring the contact angle of wetting [6]. A good wetting result can only be achieved if the oxides of solders are completely removed. A flux, normally an inorganic or organic acid, is often used to remove the surface oxides and therefore enhance wetting by solder in the molten state. For most soldering process, the effect of fluxes on the wettability of Sn/Pb alloy over various substrates has been extensively reported; however, the melting property of lead-free solders with one-dimensional nanostructures have not been reported. Also, due to the higher surface to volume ratio of nanostructures, oxidation effect may become prevail in the reflow soldering and this issue needs to be addressed.

In this paper, we present the melting behavior of nanosolder systems (tin and tin/silver alloy nanowires/nanorods) under

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Table 1
List of fluxes used in the experiment.

Flux type	Flux full name	Product name	Composition (% wt)	pH (23 °C)	Vendor
R	Rosin	Liquid flux #5 R	Rosin (50–60)	3.02 ± 0.32	Indium. Corp
RMA	Rosin mild activated	Liquid flux #5 RMA	Isopropyl alcohol (40–50) Rosin mixture (40–50)	2.74 ± 0.38	Indium. Corp
RA	Rosin activated	Liquid flux #5 RA	Isopropyl alcohol (30–40) Methyl ethyl ketone (10–30) Proprietary (1–2)	2.43 ± 0.29	Indium. Corp
Stay-clean	–	Stay Clean® Liquid soldering flux	Rosin flux (40–50) Isopropyl alcohol (35–40) Methyl ethyl ketone (10–20) Zinc chloride (<30) Ammonium chloride (5–25) Hydrochloric acid (<5)	0.29 ± 0.05	Harris Products Group

flux influence and the micron/nano-structures formed on Si substrate. We found that the flux vapor, rather than the liquid flux, can effectively remove the nanosolder surface oxide and facilitate the phase transformation and shape change of nano-solders at temperatures even below the melting point of the bulk solder materials. Under the influence of the flux vapor, an Ostwald-ripening assisted spheroid formation was observed. The micron-scale contact angle of reflowed solders was measured by direct scanning electron microscopy imaging. Finally, the effect of temperature and type of fluxes on the melting, especially the phase transition/shape change from nanowire/nanorod to spheroids was investigated.

2. Experimental

2.1. Materials and methods

Sn and Sn/Ag alloy nanowires were fabricated using polycarbonate (PC) porous membranes (Whatman) with pore size of 30 nm and 50 nm in diameter through the electrodeposition method. First, a thin layer of Ag was evaporated on one side of a commercial PC membrane by a Nano-Master NTE-3000 thermal evaporator (Nano-master, Inc.). The silver coated side of the membrane contacted with a copper plate and restrained by a glass joint with O-ring seal. After that, the membrane was filled with tin or tin/silver electrolyte and a current was applied with 15 mA/cm² density by using a potentiostat (Model 362, Princeton Applied Research). After the plating, the membrane was dissolved in dichloromethane to release the nanowires. The detailed nanowire fabrication process can be found from our previous publication [7]. Sn nanorods were synthesized by a surfactant-assisted chemical reduction method that has been developed in our group [8]. Briefly, 40 mg tin sulfate was added in 40 mL 8 mM sodium dodecyl sulfate (SDS) solution first and stirred for 10 min. Then 24 mg of sodium borohydride was added and the solution was stirred at 350 rpm at room temperature. The nanorod formed after 30 min reaction and the product was centrifuged and cleaned by DI water and ethanol for further characterization.

For a solder reflow process in electronics/microelectronics assembly, a number of factors can influence the process, including reflow profile, roughness of substrates, flux selection, quantity or volume of molten solder, reaction between the solder material and the substrate [6]. As the first attempt of studying the melting and wetting of solder nanowires and nanorods, Si wafer was chosen as a non-reactive surface to avoid the interface diffusion and reaction between the solder and substrate. Since the traditional solder paste mixed with the micron-sized solders and liquid flux (10–15 wt%) can potentially bring the difficulty in nanosolder dispersion and the surface cleaning, flux vapor was used for nanosolder reflow.

Rosin based flux, the most widely used one in electronics manufacturing, can effectively remove the oxide from metal surfaces [9,10]. There are three types of rosin based fluxes: R (rosin) is relatively low active, RA (rosin activated) is quiet strong, while RMA (rosin mild activated) is in between (see Table 1). Nowadays, the water soluble fluxes containing inorganic chemicals such as hydrochloric acid and zinc chloride have received more attention due to the easiness for cleaning; however, these types of fluxes are often more aggressive [11]. In this paper flux RMA was studied as the main focus, while the others – R, RA and water soluble flux were investigated as comparison. The rosin based fluxes were obtained from Indium Corporation of America, and the water soluble flux (also called “stay-clean” flux) was purchased from J.W. Harris Co., Inc.

The nanosolder reflow experiments were carried out in a programmable high-temperature tube furnace. The flux RMA was dropped onto a glass substrate and placed in the furnace adjacent to a Si wafer with solder nanowires/nanorods on top. Upon heating, the liquid flux was vaporized to clean up the surface oxides of the nanosolders. Nitrogen purging was used to avoid further oxidation of nanosolders during this process. The nanosolder reflow process followed the standard industrial reflow profile including preheating, thermal soak, reflow and cooling steps. The peak temperatures were controlled at 250 °C, and the time above the melting temperature of Sn (232 °C) was 5 min. Other peak temperatures were also tried, including 220 °C and 190 °C. After reflow, the rosin based flux residual on nanosolders were cleaned by iso-propanol and then dipped into 50 °C water to clean the possible salts generated during reflow, and the water soluble stay-clean flux was only cleaned by water at 50 °C for 10 min.

2.2. Materials characterization and equipments

The morphology and composition of the solder nanowires and nanorods were analyzed by a field emission scanning electron microscopy (FESEM, model JSM-7401F) which is equipped with energy dispersive X-ray spectroscopy (EDS). For oxide growth kinetic study, the tin nanowire suspensions of as-fabricated tin nanowires, nanowires stored in ethanol for one week, and nanowires stored in ethanol up to three months were dropped on three pieces of Si wafers, respectively. Then the samples were immediately loaded into the FESEM/EDS to characterize the oxide growth. The oxide thickness of nanowire and nanorod were measured by high resolution transmission electron microscopy (HRTEM) using a JEOL-2100 microscope operated at 200 kV. The pH values of different fluxes were measured three times by a Fisher Science Education pH meter and the average values were reported with standard deviation.

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