

## **MINING, METALLURGY, & MATERIAL SCIENCE ENGINEERING (MMM)**

### **MMM 200201 AGUILA, Loreto G. (MS Mat'l. Science Eng'g) Precipitation Hardening of Manganese Bronze. 2002**

The hardness of binary copper-manganese alloy was measured for two compositions, 20% Mn and 30% Mn, to determine the optimum parameters by which the alloy may be hardened. The alloy was homogenized at 800°C, where it is present as a single phase,  $\gamma$ , for one hour. A sample each was then subjected to age hardening at temperatures of 200, 300 and 400°C, and age heat treatment duration of 1, 2, 4 and 8 hours. All aged samples were furnace cooled. The study shows that composition and duration significantly affect hardness. The average hardness increased from  $H_v=118$  at 20% Mn to  $H_v=131$  at 30% Mn. The average hardness of the alloy heated for 1, 2 and 4 hours is  $H_v=120$ , whereas for heat treatment duration of 8 hours, the average hardness is  $H_v=138$ . Temperature does not have significant effect on hardness in the temperature range investigated.

At 20% Mn, hardening is controlled by transformation hardening following the reaction  $\gamma_3 = \gamma_1 + \gamma_2$ . At 30% Mn, hardening is contributed by the precipitation of  $\alpha$ -Mn, the hardening phase. Peak hardness was achieved at 8 hours of aging at 300°C, with hardness  $H_v=166$ . The alloy has overaged at 10 hours of aging when hardness dropped to  $H_v=121$ .

XRD proved insensitive in tracing the development of hardness. This is mainly due to the limited amount of  $\alpha$ -Mn present in the system, estimated to be 5% at 300°C isotherm. The peaks generated by the alloy belonging to  $\gamma$  masked peaks that could have been generated by  $\alpha$ -Mn.

Metallography was useful in identifying the presence of the second phase. This method was made on the alloy: containing 30% Mn and heat treated at 300°C, for 1, 2, 4, 8, 10 and 12 hours.  $\alpha$ -Mn started to appear in the alloy heat treated for 2 hours. They precipitated mostly at grain boundaries in the form of circular to oblong crystals. Their size grew at the rate of 4.5% per hour for the first eight hours, and at 2.5% per hour during the next four hours. After two hours of heat treatment,  $\alpha$ -Mn was measured to be from 3 to 4.5 $\mu\text{m}$  in diameter, at 12 hours, the largest dimension was measured to be 9 $\mu\text{m}$ .

To validate the results of the experiments, confirmatory studies using alloys containing 30% Mn and above (up to 40%), longer aging times (up to 12 hours) and higher aging temperatures (up to 600°C) should be pursued. Homogenization of the casting prior to cutting it into sample sections, and quenching the aged sample instead to slow cooling them may be the operational variables instituted in these future studies. Finally, a continuation of this work may concern full mechanical and physical characterization of the alloys to identify their various industrial applications.

**MMM 200302 AGRA, Francisco A. (MS Mat'l. Science Eng'g)  
Thermal Oxidation of AIAs and the Possibility of  
Confinement in an Optical Device. 2003**

The wet oxidation of AIAs layers and its ability to confine current in an optical device was investigated in this study. Two samples were grown by molecular beam epitaxy. One consists of a thick (300 nm) AIAs layer in GaAs while the other contains thin (60nm) AIAs layers in a p-i-n device employing a vertical cavity surface emitting laser structure. Fresh edges of AIAs layers embedded within the samples were prepared either by simple cleaving or by lithography patterning and etching into 225- $\mu$ m diameter mesas. Sections cut from both samples were heated in a modified wet oxidation furnace to oxidize the AIAs layers at different temperature and time values. Oxidation proceeds laterally starting from the edge. The extent of oxidation, defined as the length of oxide formed starting from the edge up to the AIAs/oxide interface, was compared for all samples.

SEM photomicrographs indicate that the formation of AIAs oxide occurred at the 430°C but the oxidation rates are too slow for fabricating oxide-confined devices. Hence, the temperature for oxidation was set at 450°C. At this temperature, the thick AIAs layer oxidizes at a faster rate compared to thin AIAs layers for both cleaved and circularly patterned samples. This is attributed to a more pronounced 'interface effect' on oxidation as the layer gets thinner. The effect of geometry on oxidation rate (e.g. cleaved vs. circularly patterned shapes) is significant at longer oxidation times ( $t > 15$  min) for thick layers at shorter oxidation times ( $< 15$  min) for thin layers. This is attributed to the increasing amount of oxidants

per unit area, or flux, at the reaction interface in cylindrically patterned AIAs layers in contrast to the decreasing flux in cleaved AIAs layers as oxidation progresses.

Two light-emitting diodes were fabricated from the p-I-n sample employing a VCSEL structure to demonstrate current confinement. The samples were lithographically patterned and wet etched into 225  $\mu\text{m}$  diameter mesas. One sample, however, was heated at 450°C for 75 minutes in a wet oxidation furnace leaving only the AIAs layers within the inner 75- $\mu\text{m}$  diameter region unoxidized. The other sample was left as is. Al metal contacts were deposited by thermal evaporation. The electroluminescence spectrum of the diodes was compared with a constant current input of 0.5 mA.

Infrared camera photographs of the oxidized device under forward bias revealed that the optical emission was confined within the unoxidized region only, proving that indeed the oxidized layer is confining the current. Furthermore, the oxidized sample yielded a total integrated intensity 9 times stronger than that of the unoxidized sample for the same current levels (~0.5mA). This is attributed to the increase in current density due to the confinement of current over a limited area defined by the oxidized AIAs layers in the oxidized sample.

**MMM 200303 AUNGON, Zenaida O. (PhD Mat'l. Science Eng'g)  
Kinetics of Self-Propagating High Temperature  
Synthesis of Silicon Carbide. 2003**

Silicon carbide produced by self-propagating high temperature synthesis from silicon powder and carbon powder. The reactant powders were modeled into pellets of 6mm diameter and 8 mm height. The SHS reaction was initiated using graphite electrodes. Ignition between 900°C and 1400°C were tested and the optimum ignition temperature obtained was 1200°C.

Mixtures of five different Si to C molar ratios were experimented. Pellets with 1:1 molar ratio or at stoichiometric proportion gave a self-sustaining reaction. The highest peak temperature monitored was 1688°C which was exhibited by pellets in stoichiometric proportion.

In terms of temperature changes, the SHS of Si + C system considered can be divided into three stages: (1) Stage I or Incubation stage, (2) Stage II or Propagation Stage, and (3) Stage III or Cooling-off stage. The incubation stage was characterized by temperature less than ignition temperature. The propagation stage was characterized by a rapid increase in temperature brought about by the exothermic reaction, which commenced upon ignition of the sample.

The typical temperature – time behavior of the system was described by the equation:

$$T = 0.0059t^3 - 0.63t^2 + 22.72t + 761.43$$

The rate of reaction was described by the equation:

$$R = \frac{dx}{dt} = 3.7 \times 10^{-6} T^2 - 0.0075T + 3.89$$

Analysis of the data showed that at 1000\degree C the rate of reaction was constant for the five mixtures considered and equal to 0.1 mm/s. the data also showed that the system was Chemical Reaction Controlled and was described by the equation:

$$F = \frac{kC_{Sib}}{p_c L} \bullet t$$

Where  $\frac{kC_{Sib}}{p_c L}$  was constant for the system and F was the fraction reacted.

The average experimental values of  $\Delta H_{298k}$  and  $\Delta G_{298k}$  for the reaction considered are -71.59 kj/mole and -68.55kj/mole, respectively.

**MMM 199904 CLEMENTE, Eligia P. (MS Met. Eng'g)  
Dissolution Kinetics of Platinum in Aqua Regia and Ammonium Carbonate Solutions. 1999**

The use of aqua regia in dissolution has been demonstrated as an effective means of rendering most metals in solution. The dissolved

species can then be precipitated out in sequence as a means of separating one from the other. In the case of gold and platinum, both of which are present as the chloride after the aqua regia dissolution, precipitation of the platinum as the chloride provides a means of isolating one from the other. The use of ammonium chloride has been a common practice, but the precipitation is rapid and sometimes causes trapping of some gold chloride. In this study, ammonium carbonate is used as a weaker base which reacts and forms an intermediate chloroplatinous phase which separates platinum from the gold.

The experiments show the reaction to be independent of agitation speed but totally dependent on the molar concentration of the leachant as well as the process temperature. The energy of activation was found to be at a low of 34.44 kJ/mole (8.23 kcal/mole) after around thirty minutes. The first order chemical reaction which controls the dissolution is governed by the reaction of the platinum metal with the hydrochloric and nitric acids in the aqua regia to produce the precipitate of platinum chloride with nitochlorous acid and water. The free energy of reaction is – 109.87 kJ (-26.76 kcal).

The initial dissolution was found to be chemical reaction controlled, but after an incubation period where the concentration of platinum in solution accumulates to around 30 ppm, the dissolution was found to progress to a second chemical reaction described by the chemical reaction of the platinum chloride precipitate with the ammonium carbonate and the nitrochlorous acid producing a yellowish-orange precipitate of ammonium chloroplatinate with hydrochloric acid and gas bubbles of nitrous oxide and carbon dioxide, with a free energy of -123.89 kJ (-29.61 kcal).

The slow first order chemical reaction controlled diffusion resulting in the formation of the platinum chloride precipitate is governed by the Spencer-Topy mathematical expression:

$$t = k'''[1 - (1 - \alpha)^{1/3}] - b$$

with a slope of  $5 \times 10^{-5}$  and an intercept equivalent to 0.001. As the concentration of the platinum chloride reaches around 30 ppm, the behavior progresses to a second chemical reaction controlled diffusion reaction governed by the same equation but with different parameters.

The slope of this equation is found to be  $1.25 \times 10^{-3}$  and its intercept 0.0875.

**MMM 199805 DE LOS REYES, Ronald Allan S. (PhD Mat'l. Science Eng'g)  
Effect of Annealing on the Nonlinear Voltage of  
Doped ZNO Polycrystalline Variable Resistor  
Ceramics. 1998**

ZnO variable resistors with as-sintered nonlinear voltage of around 23 V were heat treated in an oxidizing atmosphere at 400°C to 700°C for 1 hour to 6 hours. Results indicate that the nonlinear voltage decreases linearly with time and exponentially with the temperature when annealed between 400°C to 700°C. Annealing at 750°C and 800°C increases the nonlinear voltage. This is attributed to the creation of new Zn interstitials from Frenkel disorder defects. The estimated value of the activation energy for annealing gives further evidence to support the proposed model of diffusional elimination of Zn interstitials into the grain boundaries to stabilize the varistor devices.

**MMM 200006 DENOYO, Alvin B. (MS Met. Eng'g)  
Accelerated Weathering of Dolis Feldspar to Kaolin.  
2000**

Feldspar group of minerals is composed of aluminosilicates of potassium, sodium, calcium and occasionally barium. They are used extensively as fluxing agent in the manufacture of porcelain and glass and when polished, as semiprecious stones. When feldspars are altered by natural means, hydrous aluminum silicates known as kaolin or china clay are formed, kaolin is the principal ingredient in the manufacture of china and porcelain and is widely used in the making of papers, rubber paints and many others.

With this high demand of kaolin, many investigations were undertaken with the purpose of developing a method for feldspar alteration. Hydrothermal treatment in a reaction chamber either with hydrofluoric acid, carbonic acid or hydrochloric at elevated temperatures

and pressures proved to accelerate the weathering of feldspar. Reaction time, on the other hand, is totally dependent on what kind of environment will be used.

This study evaluates the possibility of converting feldspar to kaolin by using dilute hydrochloric acid with aluminum hydroxide. With a reactor, the sample, together with the solution are allowed to react at 350°C up to 168 hours.

Feldspar conversion of up to 92% has been obtained. Such conversion was validated by SEM-EDX, X-ray diffractometry and thermogravimetric analysis. The conversion rate was also found to be chemical reaction controlled.

**MMM 200007 DUENAS-JARLIGO, Ma. Ophelia B. (MS Mat'l. Science Eng'g)  
Synthesis of Tobermorite Using Ultrafine Geothermal  
Silica Waste. 2000**

Synthesis of tobermorite using ultrafine geothermal silica waste was conducted. Geothermal colloidal amorphous silica and its cristobalite form were used as precursors together with reagent grade CaO. The SiO<sub>2</sub> component was substituted with 0, 5, 10, and 15%  $\gamma$ -alumina to accelerate the formation of tobermorite. The mixtures were placed in autoclavable vials and had Ca/(Si+Al) ratio equal to 0.8, and with water to solid ratio equal to 2. The mixtures were then treated hydrothermally in an autoclave at 180°C or 8 hours without stirring.

The synthesis yielded Al-tobermorite and C-S-H phases. However, unreacted silica was detected for mixtures with cristobalite. The amount of tobermorite formed and the crystallinity of the synthesized material increased with increasing %Al substitution. This effect was found effective, only upon conversion of precursors to C-S-H. the colloidal silica mixtures were able to produce more tobermorite and more crystalline material than with cristobalite.

The outcome of the study is expected to reduce the danger of ground water contamination of silica, and the production and utilization of the industrially important tobermorite from geothermal silica waste.

**MMM 199708 ESTEBAN, Rommel A. (MS Mat'l. Science Eng'g)  
Moisture Absorption in Electronic Molding  
Compound. 1997**

In epoxy molding compounds used for semiconductor packaging, moisture is known to have an adverse effect on the device reliability. This study is concerned with moisture uptake as a function of temperature, relative humidity, and molding history. The effects of these variables were systematically examined for a single commercially available molding compound through moisture absorption experiments and thermal methods analyses.

The amount of moisture absorbed were significantly affected by the temperature, relative humidity, and post mold cure time. Absorption measurements showed that the transport mechanism is generally diffusion which can be characterized as Fickian in nature.

A mathematical model equation has been set-up to describe the moisture absorption of the molding compound. The equation

$$\frac{M_t}{W_o} = 0.00001 \left( \frac{\sqrt{t}}{l} \right) (RH)^{1.36} \exp\left( \frac{-2056}{T} \right)$$

was able to predict the amount of moisture absorbed accurately. This equation was consistent with Fickian diffusion process.

**MMM 199909 FLAUTA, Randolph E. (MS Mat'l. Science Eng'g)  
Characterization of Aluminum Films Deposited on  
Silicon Substrate by Radio Frequency (RF) Magnetron  
Sputtering. 1999**

A study was made to determine the characteristics of aluminum thin films deposited on p-type (111) Silicon (Si) substrate using Radio Frequency (RF) Magnetron Sputtering at different operating conditions. The parameters studied include the RF power, deposition time (DT) and operating pressure (OP). The RF power ranged from 75 to 200 Watts. The

deposition time ranged from 5 minutes for thin deposits to 2 hours for thicker deposits at varying power and pressure. The operating pressure was set at 5 and 10 mTorr. The minimum ignition pressure was set at 30mTorr and the base pressure ranged from  $4.0 \times 10^{-6}$  to  $2.0 \times 10^{-5}$  mTorr.

Surface morphology examinations were made using the Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) to determine the film thickness, surface roughness, and average grain size of the sputtered samples. The thickness monitor inside the deposition chamber was calibrated for thickness determination. This was done by etching a step on the film with HF followed by examination of the etched and unetched part by AFM. The crystal structure of the deposited film was examined using the X-ray Diffractometer. The Al film deposited exhibited preferred orientation with the (200) peak being the most dominant.

The thickness of the Al film was found to increase linearly with respect to deposition time and RF power. Increasing the operating pressure resulted to decrease in film thickness. The highest deposition rate achieved was  $90 \text{ \AA}/\text{minute}$  at RF power of 200W, deposition time of 2 hours and operating pressure of 5mTorr. Using the deposition parameters mentioned, the film thickness attained is around  $1 \text{ \mu m}$ . Thicker samples produced rougher surface. Parametric study revealed significant two-factor and three-factor interactions among RF power, deposition time, and operating pressure.

The total resistance was measured using a two-point probe wafer parametric analyzer and the sheet resistance using the four point probe setup. Using the four-point probe, it was found out that the sheet resistance of the film decreased as the film thickness was increased. For the thicker films produced, the resistivity of the Al films approached that of the bulk resistivity.

**MMM 199910 GONZALES, John Ivan J. (MS Mat'l. Eng'g)  
Moisture and Thermal Degradation of Cyanate-Ester-  
Based Die Attach Material. 1999**

Cyanate-ester-based thermosetting die attach material, commonly known as Low Temperature Die Attach (LTDA) are the newest innovation

in Hermetic Die Attach Technology due to their improved manufacturability, high decomposition temperature and a moisture gettering effect. Although their dispensability and decomposition temperatures are well documented, little information is available on the effects of prolonged exposure to moisture and thermal conditions. A study was therefore conducted to investigate the behavior of cyanate-ester under different thermal and moisture environments.

Results of the experiment showed that the cyanate-ester initially exhibits weight loss and subsequent weight gain after prolonged exposure. The moisture saturation (maximum weight gain) recorded was around 0.12% of the initial weight. Incorporation of the moisture into the polymeric structure was verified by Infrared Spectroscopy. Differential Scanning Calorimetry (DSC) revealed an exothermic heat of -96.74J/g in the cyanate-ester curing. Thermo-gravimetric analyses (TGA) of cured samples exposed to different environments suggested a simultaneous evolution of adsorped moisture and carbon dioxide.

Die shear strength of two different die sizes was observed to degrade exponentially with exposure time. For the 224x225 mil die, the time-to-failure equation as a function of temperature and humidity was established to follow the model

$$t_f \cong A(\%RH)^n \exp(\Delta E / kT)$$

where

$$A = 1.001 \times 10^{-5}; n = -23.45 \text{ and } \Delta E = 0.362 \text{ eV}$$

The same model was also established for the 65x75 mil die with parameters  $A$ ,  $n$  and  $\Delta E$  equal to 0.112, -3.83, and 0.09eV, respectively.

Calculations of die shear strength time-to-failure for the exposure to shop floor condition (25°C/55%RH) are also presented.

**MMM 200011 LANTICSE, Leslie Joy G. (MS Met. Eng'g)  
Surface-Chemical Separation of Finely-Dispersed  
Mercury in Aqueous Solution. 2000**

In small-scale gold mining industries, relatively high concentrations of mercury, 284 ppm, were found in the waste water and solid material. Minute droplets of mercury were found suspended in the waste water and significant amounts of mercury were mixed in the waste sand material. More than 100,000 small scale miners are distributed all over the country.

Surface-chemical separation is a technology used to recover colloid materials from its suspending medium by utilizing the surface characteristic of the materials involved. This method effects heterocoagulation between materials thus facilitating recovery or collection. This study will focus on the treatment of the waste water of the small scale mining industries which contains suspended colloids of mercury.

Mercury when submerged in an aqueous solution exhibits a negative surface charge. Aluminum oxide, on the other hand, generally exhibits a positive surface charge over a wide range of pH condition. Its isoelectric point (iep) occurs at pH 9.7. By allowing the suspension of mercury to pass through a column bed of aluminum oxide, heterocoagulation occurred at various contact points of the two material. As high as 98.2% recovery was obtained with this technology.

In conclusion, aluminum oxide fiber is a material with potential for use in the recovery of mercury from the suspension. i.e., waste water of the small-scale mining operation. However, any material that exhibits a positive surface charge can be a potential collector using the same technique. Furthermore, the study of indigenous materials which are cheap and locally available is recommended for practical use to the small-scale miners.

**MMM 200012 MADRID, Pepe L. (PhD Mat'l. Science Eng'g)  
Mathematical Modeling of Implant Dose and  
Characterization of P-N Junctions Formed by Ion  
Shower Technology (IST). 2000**

Ion Shower technology is a recently developed technique pf introducing impurities into silicon wafers to form p-n junctions. The

process of introducing impurities or dopants is done under the ion shower implantation system. From single crystal silicon wafers (n-type and p-type) p-n junctions were formed using boron and phosphorus atoms as impurities. The p-n junctions were characterized to develop a model that would predict the amount of impurities implanted in relation to the ion beam current and doping time as variables. A planar diode was also fabricated and characterized. Results showed that implanted impurities obeyed very well the Gaussian profile distribution as the impurities diffused into the substrate upon annealing. A mathematical formula was also determined for both boron and phosphorus atoms that related the implant dose with ion beam current and doping time. The determined formulae were as follows:  $Q = 5.2 \times 10^{12} I * t$ , for phosphorus, and  $Q = 3.1 \times 10^{11} I * t$ , for boron. A diode ideality factor of almost 1.0 was obtained from the expanded I-V characteristic curve, which could be considered as a great improvement over the previous works done by other researchers.

**MMM 199813 NUÑEZ, Ricarte C. (PhD Mat'l. Science Eng'g)  
Fatigue Behavior and NDE Characteristic of  
Aluminum Silicon-Carbide Metal-Matrix Composites  
Using Ultrasonic Pulse-Echo Method. 1998**

Discontinuous SiC particulate-reinforced aluminum alloys are metallic-based composites belonging to a class of advanced materials that are suited for applications requiring high performance, isotropic mechanical properties. In this study, S-N plots were obtained from the results of fatigue tests done in tension-tension which were performed on monolithic aluminum and composite samples having notch radii of 26 cm and 1.6 mm at different stress levels. The results showed that the composites were superior in the strength than their monolithic counterparts. The effect of notch radii in these samples during the fatiguing process were evaluated and a nondestructive ultrasonic pulse-echo method employed in this study resulted in the determination of the behavior of the bulk wave velocities and elastic constants in these samples at different states namely- pre-fatigue, in-fatigue and post-fatigue states. Micrographic examinations revealed the presence of dimples that caused failure in the samples. The sensitivity to fatigue of the bulk wave

velocities and elastic constants were observed in both monolithic aluminum and its composite counterpart and the comparison of the results obtained from the fatigue tests and nondestructive methods were also presented.

**MMM 200214 OCONER, Irmin S. (MS Mat'l. Science Eng'g)  
Post-Quench Staging Time Behaviour of Cryogenically  
Treated Tool Steel. 2002**

Conventional heat treatment of high alloy steel involves the process of heating the metal above the austenitizing temperature, soaking and quenching either in oil or air. During cooling, once the temperature has reached room temperature, it is then tempered in the furnace to impart toughness, improve dimensional stability, relieve residual stresses and develop secondary hardening and red-hardness property for hot-work and high-speed steels. Usually, tempering of tool steels is done twice in order to eliminate the presence of retained austenite. Presence of retained austenite is detrimental because of its ability to transform to martensite when heated. The effect of this transformation produces tremendous difficulty in the control of the dimension due to the crystallographic expansion of austenite to martensite (approximately 4% by volume).

In the experiment, the % retained austenite as affected by two time variables; namely: time of post-quench stage soaking at room temperature and time of soaking in liquid nitrogen after post-quench stage soaking at room temperature were investigated. A total of 44 samples of AISI D2 (1.5% C, 12% Cr) tool steel were prepared, then, austenitized and quenched in oil. At room temperature, the samples were soaked at different time intervals (0, 1, 2, 9, 20, 49, 81, 121, 144, 196, and 225 hours). At the end of each post-quench staging time, the samples were soaked in liquid nitrogen at different times (1, 8, 16, and 24 hours). X-ray diffractometer was used to measure the retained austenite that transformed to martensite. From the data plots, the variation of % retained austenite with either soaking time or post-quench staging time showed a linear relationship. The effect of either one of the independent variables (soaking time in liquid nitrogen, post-quench staging time at room

temperature) appeared to be dependent on the level of the other independent variable, implying an interaction between the two. The dependence of this effect on the level of the other variable can be summarized as follows:

- Empirical relationship between *effect of post-quench staging time on % retained austenite* and *soaking time*:

$$y = -0.0028x + 0.0453$$

where  $y$  = effect of post-quench staging time at room temperature (in % retained austenite/hr) and  $x$  = soaking time in liquid nitrogen in hours

- Empirical relationship between *effect of soaking time in liquid nitrogen on % retained austenite* and *post-quench time at room temperature*:

$$y = -0.0037x + 0.3284$$

where  $y$  = effect of soaking time in liquid nitrogen (in % retained austenite/hr) and  $x$  = post-quench staging time at room temperature in hours

The results show that the effects of post-quenched staging time at room temperature or soaking time are initially positive from 0 to 49 hours followed by an essentially linear decrease of the effect with time to a negative value for sufficiently longer times. A positive effect initially indicates that the treatment has a stabilization effect, a condition by which retained austenite no longer transforms to fresh martensite. The effect, however, indicated that at long post-quench soaking times, the stabilization effect on austenite is hindered and the retained austenite is transformed to martensite. This now favors a more dimensionally-stable tool steel.

**MMM 200315 PUNZALAN, Jaime C. Jr. (MS Mat'l. Science Eng'g)  
Understanding the Effect of Surface Flaws on  
Fracture of Silicon Die. 2003**

An integrated circuit (IC) silicon die experiences different thermomechanical stresses during assembly, test, mounting, and application. Ideally, the silicon dice is expected to withstand stresses induced during normal processing and application. But it is not uncommon for standard assembled package and flip chip package to fail due to silicon die cracking. As the industry continues to develop smaller and thinner silicon dice to fit the ever shrinking IC unit, understanding of the failure mechanism becomes more important.

Surface flaws often encountered in high volume manufacturing environment of plastics assembly were simulated using high automated equipment in semiconductor packaging. Two experiments were undertaken: i) varying sizes of ejector pin damage induced by different set-ups on bonded (111) wafer and 2) a  $2^k$  factorial experiment with background, saw, ejector pin damage as factors on a standard (111) wafer. The fracture strength of the silicon dice with surface flaws were measured using four-point bend test and quantified as a function of degree of surface damage. Samples were splitted at DTFS to determine the effect of fulcrum stress due to debris. Effect of surface flaws on silicon fracture strength was validated using thermal stress test. Finally, fractography of silicon samples established whether the failure was influenced by the presence of surface flaws.

Fracture strength measurements through four-point bend test were correlated with the reliability stress based on average readings, standard deviation, and failure mode. The critical crack size for bonded wafers was determined to be 36.5 x 8.41 x 4.0 microns which was the smallest tool mark measured from lots with failures at reliability test. For the factorial experiment on standard wafers, it was found out the backgrind surface finish and ejector pin damaged had the highest effect on fracture strength.

Based on the reliability test results, fulcrum stress at DTFS did not pose any reliability risk if there was no surface damage on the silicon dice. The fulcrum stress was generated by debris that neither caused package crack nor left any tool mark. On the other hand, silicon with surface flaw showed failures. Failure rate at thermal shock test of silicon with surface damage increased when subjected to fulcrum stress.

Through fractography of fracture surfaces, the influence of surface flaws on the mechanism of crack propagation was verified. Further study of silicon that were used in fracture strength testing and from units that failed in reliability tests revealed distinct fracture surface features for the different thermal stress test performed.

**MMM 200216 ROMANES, Maia C. (MS Mat'l. science Eng'g)  
Surface Restoration of Corrosion Pits in 316L  
Stainless Steel Through Modified Metal Injection  
Molding. 2002**

Pitting corrosion represents a critical failure mechanism in stainless steel structures, as it may lead to structural failure even with negligible loss in metal weight. In 316L stainless steels, pitting creates highly convoluted single-mouthed cavities whose walls consists of convex and concave surfaces of high surface energy. These cavities eventually penetrate through the thickness of the metal causing failures in container applications. This study investigated the use of very fine metal powder as filler material to repair stainless steel surfaces that have been attacked by pitting corrosion. Pits were infiltrated under pressure within a molten feedstock consisting of metal powder and polymeric binder through a modified Metal Injection Molding (MIM) process.

The samples underwent pitting corrosion simulation in 6% FeCl<sub>3</sub> solution for 72 hrs., injection (250-kg load at 150°C) and wicking debinding (120hrs). However,, processing times were varied for binder burnout and sintering. One-hour burnout times resulted in pit-mouth fillers that failed to densify and are spongy while 6-hr burnout times resulted in mouth filler that underwent considerable densification resulting in pit-mouth restoration. The amount of binder residue and the single-mouth configuration of pits were found to be important factors that interact to produce these results. One-hour sintering time was found to be sufficient in densifying pit mouth filler. Longer sinter times result in over-aging of the samples' surface but was beneficial to inner filler by promoting neck-formation and coalescence among particles, coalescence of voids toward the middle of the pits, and movement of the inner filler toward the pit walls.

**MMM 200317 SERATE, Duane G. (MS Mat'l. Science Eng'g)  
The Correlation of Crude Corrosivity in Different Field  
Service Environments with Hydrogen Flux  
Measurements. 2003**

This study [provides the theoretical analysis and the field result of a prototype real-time portable hydrogen collector method, called Hydrosteel®. This instrument detects and measures the hydrogen diffusion through steel, as a result of naphthenic and acid corrosion (NAC) from high Total Acid Number (TAN) crudes:



High TAN crudes (TAN>1) are identified with high potential margins but are considered high risk of causing NAC during refinery processing. Five corrosion loops were studied in the Crude Distilling Unit (CDU). The hydrogen flux results were correlated with the crude oil characteristics, process conditions, and with other corrosion mechanism called Sulphidation that occurs simultaneously at the same process conditions:



The Hydrosteel portable hydrogen collection method was able to demonstrate that high flux readings could be obtained on a system that is expected to be corrosive, and demonstrated that high hydrogen permeation readings could indeed be detected, and correlated to the prevailing process conditions. Good correlation was achieved for the hydrogen activity with the total acid number (TAN), crude existing sulfur content, crude fraction sulfur content, crude existing and potential H<sub>2</sub>S, % yield of the crude, and the CDU throughput. The work was able to shortlist the corrosion hotspots for NAC-sulphidation in the crude distiller unit, from five corrosion loops known theoretically to have NAC-sulphidation, down to two corrosion loops: the Transfer Line, and the Heavy Gasoil (HGO) Stream. This is consistent with the other studies pointing to these areas as the locations where NAC is most active.

**MMM 199618 SIMEON, Arvin G. (MS Met. Eng'g)  
Extraction and Recovery of Cerium from San Vicente,  
Palawan Heavy Mineral Panned Concentrate Samples.  
1996**

Sometime in 1990-1991 a rare earth geochemical survey was conducted by the Philippine Nuclear Research Institute (PNRI) in the Northern Palawan area. PNRI have successfully delineated areas with possible rare earth deposit and it is to this reason that the study on leaching Cerium out of their mineral find had been proposed and executed.

This study tested the conventional ways such as the: Sulfuric Acid Leaching and the Caustic Leaching processes to decompose the minerals contained in the samples from Ombo, San Vicente, Palawan and transfer Ce and other rare earth elements into the aqueous solution. Further to this, included in the study is the trial precipitation of crude Cerium Oxide, completing the extraction and recovery process. Leaching is the usual route rare earth elements are extracted and recovered from their minerals. Never have it been heard of being smelted directly from its concentrate.

Results of the study suggests that opening up with sulfuric acid diluted with a certain amount of water offers the most straight forward alternative process and the best encouraging results. Chemical decomposition of Allanite ((Ce,Ca,Y)<sub>2</sub>SiO<sub>3</sub>AlOH), the main rare earth containing mineral found, to SiO<sub>2</sub>, CaSO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub> and rare earth metal ions is the key to rare earth dissolution.

Precipitation of the Cerium Oxide by NaCl-NaOH-KMnO<sub>4</sub> treatment proved to have low recovery. From 62.30% leach recovery overall recovery up to precipitation went down to 40.46%. This is equivalent to 64.94% precipitation recovery. The Cerium content of the precipitate is at 61%. The precipitation test done, however, is just exploratory in nature and is recommended for further studies.

**MMM 199719 STA. CLARA, Claude Gregory M. (MS Met. Eng'g)  
Portland Cement Raw Mix Burnability Improvement  
Using Fine-Grained Quartz as a Silica Source. 1997**

This study dealt with the improvement of Portland cement raw mix burnability of Bacnotan Cement Corporation (Quirino, Bacnotan, La Union) line number 2.

The difficulty in burning cement raw mix is often blamed on chemistry, while kiln feed coarseness is frequently ignored. *Eqn. C.1* shows that free-lime can be estimated (Theisen<sup>13</sup>) using knowledge about the clinker chemical composition (**LSF, Ms**) and the content of coarse particles in the raw mix ( $C_{125}$ ,  $Q_{45}$ ,  $A_k$ ). Theisen<sup>13</sup> states that raw mix with good burnability should have at most 3.5% free-lime at 1400°C

$$\begin{aligned} \text{*}\%f\text{-CaO}_{1400^{\circ}\text{C}} &= 0.343 (\text{LSF} - 93) + 2.47 (\text{Ms} - 2.3) \\ &+ 0.10 C_{125} + 0.83 Q_{45} + 0.39 A_k \end{aligned} \quad (\text{C.1})$$

Initial investigation showed that kiln feed coarseness is the main cause of poor burnability, most of which is due to coarse quartz particles, **Q<sub>45</sub>** (rich in coarse-grained crystals). Burnability was improved but was not economically feasible. Also, **Q<sub>45</sub>** remained significant.

Results indicate that changing the present silica source rich in coarse-grained quartz crystals with a source containing 100% fine-grained quartz crystals reduces the influence of **Q<sub>45</sub>**, improves raw mix burnability, has good economic potential, and significantly lowers the optimum fineness.

It is believed that optimum fineness is mostly influenced by the amount of coarse particles in the raw mix. For mixes using silica sources rich in coarse-grained quartz crystals, **Q<sub>45</sub>** was found to be the limiting factor. For mixes using silica sources with 100% fine-grained quartz crystals,  $A_k$  was found to be the limiting factor.

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\*where  $\%f\text{-CaO}_{1400^{\circ}\text{C}}$  is the estimated raw mix burnability at 1400°C; LSF is the clinker lime saturation factor; Ms is the clinker silica modulus;  $C_{125}$  is the calcite content in the mix ( $\geq 125\mu\text{m}$ );  $Q_{45}$  is the coarse quartz content in the mix ( $\geq 45\mu\text{m}$ ); and  $A_k$  is the silica content in the mix (non-quartz  $\geq 45\mu\text{m}$ ).

**MMM 200220 VELASCO, Angelito A. (MS Mat'l. Science Eng'g)  
Parametric and Kinetic Study of Silicon Nitride Film  
Deposition on Silicon Wafer by Low Pressure  
Chemical Vapor Deposition (LPCVD) Method. 2002**

Silicon nitride films were deposited on polished silicon wafers by low pressure chemical vapor deposition (LPCVD) method. Reaction gases were ammonia (NH<sub>3</sub>) and 20% silane (SiH<sub>4</sub>) in nitrogen. The effects of (A) deposition temperature (800, 850, 900°C), (B) chamber pressure (4, 5, 6 torr), (C) NH<sub>3</sub>-SiH<sub>4</sub> flowrate ratio (33, 66, 99) and (D) deposition time (20, 40, 60 min.) on the thickness and morphology the film produced were studied using a full 2<sup>4</sup> factorial design. The film thickness was found to increase proportionally with temperature, pressure, and time, and inversely with NH<sub>3</sub>-SiH<sub>4</sub> flowrate ratio. From the analysis of variance (ANOVA) it was found that all the main effects were statistically significant at 99% confidence levels. Also found significant at 99% confidence level were the following interactions: (1) temperature and NH<sub>3</sub>/SiH<sub>4</sub> flowrate ratio, (2) temperature and time, and (3) NH<sub>3</sub>/SiH<sub>4</sub> flowrate ratio and time. An interactive first order model was fitted to the experimental data:

$$Y = 158.46 + 70.39X_1 + 26.86X_2 - 66.44X_3 + 74.45X_4 - 29.3X_1X_3 + 33.35X_1X_4 - 30.68X_3X_4$$

where Y=film thickness in nanometers

X<sub>1</sub>=deposition temperature, coded variable= (temperature in °C - 850)/(50)

X<sub>2</sub>=chamber pressure, coded variable= (pressure in torr - 5)/2

X<sub>3</sub>=ammonia/silane flowrate, coded variable= (ratio-66)/33

X<sub>4</sub>=deposition time, coded variable= (time in minutes -40)/20

This model was found to adequately fit the experimental data. The lack-of-fit error was found to be insignificant at 95% confidence level, at the SSR/SST ratio was equal to 0.965. 2-D and 3-D plots were generated using this mathematical model.

A kinetic study was also conducted in order to determine the rate equation for the growth of silicon nitride on silicon using a chamber pressure of 6 torr and  $\text{NH}_3/\text{SiH}_4$  flowrate ratio of 99. The computed activation energy was 21.454 kcal/mol, which indicates that the surface reaction is rate limiting. The rate equation was:

$$\text{Deposition rate, nm/min} = 37661.7 \exp(-4578.5/T)$$

Scanning electron micrographs show that the silicon nitride deposits appear as spherical cap shaped clusters. The maximum diameter of the clusters increases linearly with the film thickness. Factors which tend to increase the film thickness such as temperature, pressure, and time also increase the cluster diameter. Increase in ammonia-silane flowrate ratio decreases the cluster diameter.

Energy dispersive x-ray (EDX) analysis confirms the presence of nitrogen in the film. Oxygen was also detected and was attributed to the extraneous  $\text{SiO}_2$  layer between the substrate and the  $\text{Si}_3\text{N}_4$  film.

X-ray diffraction (XRD) analysis shows that the as-deposited film was amorphous. After annealing in air at  $1400^\circ\text{C}$  for 4 hours, peak of  $\alpha\text{-Si}_3\text{N}_4$  were obtained confirming the formation of silicon nitride. Film oxidation was also observed as shown by the  $\text{SiO}_2$  peaks.

**MMM 200321 VENEZUELA, Jeffrey DG. (MS Met. Eng'g.)  
Thermal Stability Study on Titanium Disilicide ( $\text{TiSi}_2$ )  
Thin Films with Titanium Nitride (TiN) Capping. 2003**

Titanium disilicide,  $\text{TiSi}_2$ , has been largely used in semiconductor devices due to its low resistivity and good thermal stability. However, there is still a need to understand some of the factors that affects the silicide's behavior at elevated temperature. This study aims to analyze the thermal stability of titanium silicide when capped with titanium nitride.

Two types of silicide samples, one uncapped and another capped with TiN, were obtained and initially characterized. The samples were then annealed at 950°C for varying annealing times. Post-characterization were done using AFM, optical microscope and SEM to view morphological changes associated with thermal degradation. The AFM was also used to quantify the surface roughness of samples. The four-point probe was employed to monitor the changes in sheet resistance with annealing time. Lastly, EDS and XRD was used to monitor the movement of materials during thermal exposure.

Morphology analysis of the surface using AFM, FESEM and optical microscope showed progressive degradation of the surface with increasing annealing time. The uncapped sample's morphology was observed to change more drastically than the capped sample. Four-point probe analysis indicates an increase in the sheet resistance of samples with annealing time which is correlated with agglomeration and island formation in the silicide. A more drastic increase in sheet resistance was observed in the uncapped sample than in the capped one. RMS roughness measurement of the surface indicates an essentially linear increase in roughness with time especially in the early stages of degradation. A higher rate of roughening was also observed in the uncapped sample than in the capped sample. XRD and EDS analysis indicates the absence of the TiN cap from the surface after annealing.

All of these results indicate better thermal stability in the capped than in the uncapped sample. The efficacy of TiN in increasing the thermal stability of  $\text{TiSi}_2$  appears to originate from a retardation of grain boundary diffusion in the silicide.