
Highlights from Recent Literature

1 ANALYTICAL

1.1 *X-ray Fluorescence Spectrometry as an Alternative to Cupellation for Gold Determination in Jewellery Gold Alloys*

A. Marucco and W. Stankiewicz, C.N.R. – TEMPE, Istituto per la Tecnologia dei Materiali e dei Processi Energetici, Milan, Italy and Institute of Non-Ferrous Metals, Gliwice, Poland have determined the chemical compositions of 27 ternary Au-Ag-Cu alloys and quaternary Au-Ag-Cu-Zn or Pd alloys using XRF spectrometry by developing a mathematical method for the correction of the matrix effects for the analysis of Au, Ag, Cu, Zn, Pd and Ni (*Precious Met.*, 1998, **22**, 15-27). The analytical performance was tested by measurements conducted on sixteen certified gold reference materials and the results were compared to those obtained by cupellation-ICP spectrometry as well as XRF spectrometry by using empirical curves.

The experimental results indicated XRF spectrometry is an advantageous alternative to the traditional cupellation method to be used in selected cases for determining the gold concentration in gold alloys with an accuracy of close to one part per thousand. The versatility of this technique is higher than cupellation, since all alloying elements are determined simultaneously allowing certification of the entire alloy composition. Also, the XRF spectrometry analysis of tens of jewellery grade or other gold alloys based on one series of standards only considerably simplifies the calibration procedure. The impact of the method on speed of analysis and quality of data produced is discussed (see also *Gold Bull.*, 1998, **31**, 71, 119).

1.2 *Intensity Ratio Method for the Recognition of Gold-Plated Jewellery and for Gold Thickness Measurement*

R. Zheng, J. Huang, W. Zhang and Y. Li of the Fujian Institute of Testing Technology, Fuzhou, P. R. China (*Fenxi Ceshi Xuebao*, 1998, **17**, 16-19) have used the intensity ratio of two lines $L\beta$ and M in the X-ray excitation spectra of gold to distinguish gold-plated jewellery from carat gold jewellery as well as to determine the thickness of gold coating. The gold-coating thickness range detected was ca 0.4 μm with relative error of less than 15%.

2 CATALYSIS

2.1 *Preparation of Supported Gold Catalysts for Low-Temperature Carbon Monoxide Oxidation via 'Size-Controlled' Gold Colloids*

Catalytically active gold model catalysts have been prepared using 'size-controlled' gold colloids of 2 nm mean particle size by J.D. Grunwaldt, C. Kiener, C. Wögerbauer and A. Baiker, Laboratory of Technical Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, Zurich, Switzerland (*J. Catal.*, 1999, **181**, 223-232). They were prepared by reduction of chloroauric acid with tetrakis-(hydroxymethyl)phosphonium chloride in an alkaline solution, followed by adsorption of the resulting colloids onto TiO_2 and ZrO_2 at a pH lower than the isoelectric point of the metal oxides.

Analysis of the dried catalysts by XRD and HRTEM showed that the particle size was nearly preserved during the immobilization process. Only in the case of high-loadings (16.6wt%, compared with the calculated nominal monolayer coverage of 45-55wt%) did incomplete adsorption occur, affording more inhomogeneous dispersion and some aggregation. After calcination at 673 K, both zirconia- and titania- based catalysts containing 1.7 wt% gold exhibited high activity in low temperature carbon monoxide oxidation. The particle size on both supports was similar but Au/ TiO_2 showed significantly higher activity than Au/ ZrO_2 . The uncalcined Au/ TiO_2 also exhibited high activity, whereas the uncalcined Au/ ZrO_2 was inactive under the same conditions, indicating that not only the gold particle size but also the support plays a key role in carbon monoxide oxidation.

2.2 *Oxidation of Carbon Monoxide on Gold-Covered Pt(335)*

D.C. Skelton, R.G. Tobin, D.K. Lambert, C.L. DiMaggio and G.B. Fisher of the Center for Sensor Materials, Michigan State University, East Lansing, USA (*J. Phys. Chem. B*, 1999, **103**, 964-971) have studied the adsorption and reaction of oxygen and carbon monoxide on a stepped platinum surface with varying amounts of gold using TPD, TPR, LEED, and steady-state reaction measurements. When the

surface is fully covered with gold it is inert to oxygen adsorption and to carbon monoxide oxidation, and supports only a single weakly bound CO adsorption state. A stepped platinum surface, partially covered with gold exhibits new absorptive and catalytic behaviour different from those of either bare platinum or pure gold surfaces. These properties may help to explain the performance of exhaust gas sensors with Pt/Au electrodes. Unlike its behaviour on bare platinum, adsorbed CO does not completely block all the sites at which oxygen dissociates on this surface.

2.3 Study of Gold Species in Iron-Oxide-Supported Gold Catalysts Derived from the Gold-Phosphine Complex $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ and as-Precipitated Wet $\text{Fe}(\text{OH})_3^*$

The work of the University of Tokyo Department of Chemistry group reported previously (*Gold Bulletin*, 1999, **32**, 31) has now been extended (A.P. Kozlova, A.I. Kozlov, S. Sugiyama, Y. Matsui, K. Asakura and Y. Iwasawa, *J. Catal.*, 1999, **181**, 37-48) to the study of iron-oxide-supported gold catalysts, prepared by supporting a gold phosphine complex $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ on as-precipitated wet iron hydroxide $\text{Fe}(\text{OH})_3^*$ (* = as precipitated), followed by temperature-programmed calcination. The $\text{Au}/\text{Fe}(\text{OH})_3^*$ catalysts calcined at 573-773 K showed extremely high catalytic activity for carbon monoxide oxidation at temperatures as low as 203-253 K.

Interaction of the $\text{Au}(\text{PPh}_3)(\text{NO}_3)$ gold precursor with the $\text{Fe}(\text{OH})_3^*$ when adsorbed, transformation of the precursor during the heat treatments, and the state of the gold in the catalysts were studied by FTIR, XRD, TEM, XPS, and EXAFS. The gold precursor dissociated on the $\text{Fe}(\text{OH})_3^*$ surface to produce $[\text{Au}(\text{PPh}_3)]^+$ species which partially decomposed at 473 K and was transformed to small gold metallic particles with coordination numbers of 7.4-8.0 for the Au-Au bond at calcination temperatures of up to 573 K. In contrast, decomposition of the gold complex over crystalline Fe_2O_3^* resulted in large gold particles. The $\text{Au}/\text{Fe}_2\text{O}_3^*$ sample was inactive at 203-253 K and exhibited very low activity for CO oxidation at room temperature. The efficiency of the as-precipitated wet $\text{Fe}(\text{OH})_3^*$ as a support is explained in terms of a higher stability of $[\text{Au}(\text{PPh}_3)]^+$ on the $\text{Fe}(\text{OH})_3^*$ as compared to the Fe_2O_3^* due to more effective interaction of the gold species with OH groups and defects of the amorphous $\text{Fe}(\text{OH})_3^*$ surface. The results demonstrate the importance of support-metal precursor interactions, both upon supporting and during

calcination, in the formation of highly active catalysts with small gold particles for low-temperature carbon monoxide oxidation.

2.4 Kinetics of the Selective Low-Temperature Oxidation of Carbon Monoxide in Hydrogen-Rich Gas over $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$

Selective carbon monoxide oxidation was studied in simulated reformer gas by M.J. Kahlich, H.A. Gasteiger and R.J. Behm (*J. Catal.*, 1999, **182**, 430-440). Using $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ as catalyst in simulated reformer gas, quantitative evaluation of carbon monoxide oxidation rates as a function of CO and O_2 partial pressure at 80°C gave reaction orders with respect to CO and O_2 of 0.55 and 0.27 respectively. The apparent activation energy for this reaction evaluated over 40 – 100°C is 31 kJ mol⁻¹. The reaction order α_{CO} is strongly temperature dependent, due to the weak adsorption of carbon monoxide on the gold particles. Comparison with the commonly used Pt/ $\gamma\text{-Al}_2\text{O}_3$, which has an optimum operating temperature of 200°C, demonstrates that $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ already offers comparable activity and selectivity at 80°C. The authors claim that the high activity and selectivity demonstrated for $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$ make this an attractive catalyst for carbon monoxide oxidation in fuel cell applications.

2.5 Gold Catalyst for Fuel Cells

V.M. Tatchev of the Laman Consultancy Ltd, Bulgaria has filed a patent (WO Patent 9916546 A1 990408) claiming the use of gold catalyst for reforming and electrochemical oxidation of hydrocarbon fuels, methanol, and methane, for application in the fuel cell industry. The gold catalyst is suitable for removal of impurities from the anodic fuel, by selective oxidation of the carbon monoxide. The active component of the catalyst is a complex which consists of gold and reducible oxide from the transition metals group. The concentration of the gold is from 0.1 to 2.5% and that of the transition metal is from 0.1 to 5%. The catalyst support consists of ceria, zirconia and titania and the working temperature of the catalyst is from ambient to 650°C.

2.6 Supported Gold Catalysts Prepared by Using Nano-Sized Gold Particles Dispersed in Nylon-11 Oligomer

Gold supported on titanium oxide has been prepared by using nano-sized gold particle/nylon-11 oligomer composites (K. Sayo, S. Deki and S. Hayashi, Faculty of Engineering, Department of Chemical Science and

Engineering, Kobe University, Japan, *J. Mater. Chem.*, 1999, **9**, 937-942). The catalyst was prepared by vapour-deposition of gold onto a nylon-11 oligomer film followed by heat treatment. The gold particles/nylon-11 oligomer composite was adsorbed rapidly on the surface of TiO₂ and calcined at various temperatures in air, to give nano-sized gold particles on the surface of TiO₂ without coagulation. The catalytic activity of the gold particles for the oxidation of carbon monoxide was measured in a flow reactor. When the calcination was carried out in two stages (the first at 500°C in vacuum, and the second at 400°C in air), the growth of the size of the gold particles was suppressed considerably, and the supported gold catalyst thus obtained showed very high activity for the oxidation of carbon monoxide, with a temperature of -10°C for 50% conversion of CO.

3 CHEMISTRY

3.1 *First Examples of Gold Thiocadmates: A₂Au₂Cd₂S₄ (A = Rb, Cs) and K₂Au₄CdS₄: Bright Photoluminescence from New Alkali Metal/Gold Thiocadmates*

The synthesis of Cs₂Au₂Cd₂S₄, Rb₂Au₂Cd₂S₄, and K₂Au₄CdS₄ in reactive A₂S_x (A = K, Rb, Cs) fluxes at 550°C is reported by E.A. Axtell and M.G. Kanatzidis, Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, USA (*Chem.-Eur. J.*, 1998, **4**, 2435-2441). Cs₂Au₂Cd₂S₄, and Rb₂Au₂Cd₂S₄ are new layered compounds which feature the linear [Cd₂S₄]_n⁴ⁿ⁻ fragment, connected in layers by linearly coordinated Au atoms. K₂Au₄CdS₄ is assembled from single [CdS₄]⁶⁻ tetrahedra which are arranged in a rectangular lattice and linked by four linearly coordinated Au(I) atoms. There are two sets of 1-dimensional (AuS)_nⁿ⁻ chains in K₂Au₄CdS₄, running in the (110) and (-110) directions and stitched together with tetrahedrally coordinated Cd atoms. The A₂Au₂Cd₂S₄ compounds and K₂Au₄CdS₄ are wide band-gap semiconductors and photoluminesce strongly. The optical absorption and photoluminescence properties are reported.

3.2 *Gold and its Compounds*

A review on gold and its compounds, with 131 references, edited by W. Hiller, C.E. Zybill and W.A. Herrmann, Anorganisch-chemisches Institut der

Technischen Universität Munchen, Germany, has been published in *Synth. Methods Organomet. Inorg. Chem.*, 1999, **5**, 55-108.

4 COATINGS, FILMS, MEMBRANES AND WIRES

4.1 *Gold Liquids for Decorative Coatings with Good Alkali Resistance*

The NE Chemcat Corporation has filed a patent (S. Sato and H. Hamada, Japanese Patent 11006072 A2 990112) to cover decorative gold coatings. The gold liquids contain organic compounds of Au, Rh, and Bi, and resins, in organic solvents. The gold liquids are coated on decorative substances and then fired. The gold-coated decorative products with good resistance to alkaline detergents are suitable for dishes for automatic washing machines.

4.2 *Nonaqueous Gold Colloids. Investigations of Deposition and Film Growth on Organically Modified Substrates and Trapping of Molecular Gold Clusters with an Alkyl Amine*

F. Tian and K.J. Klabunde (Department of Chemistry, Kansas State University, Manhattan, USA, *New J. Chem.*, 1998, **22**, 1275-1283) have prepared gold-acetone colloidal solutions by a metal vapour co-deposition procedure (solvated metal atom dispersion). Gold films were prepared by allowing adsorption / deposition on (sulfanylpropyl)trimethoxysilane, (aminopropyl)trimethoxysilane or (*iso*-butyl)-trimethoxysilane-modified substrates. The mechanism of gold film formation was studied by AFM and TEM.

At short contact times, self-assembly of colloidal gold particles onto the functionalized substrate surfaces took place and both individual particles and aggregates appeared. As contact time increased, a dynamic equilibrium was evident on the thiol- and amine-modified substrates and resulted in the development of more stable, close-packed layers. At still longer contact times, a smooth film was formed on the surface. In addition to film growth studies, the gold colloid particle growth in acetone was studied. By adding dodecylamine, particle growth was stunted and very small (2-3 nm) individual crystallites coated by the amine were obtained. These materials were molecular in the sense that they could be precipitated and redissolved many times without change. TEM data showed that the particles were spatially separated and the interparticle spacing was dependent on the amount

of dodecylamine present. The FTIR data indicated that a significant amount of amine (N-H bond) and acetone (C=O bond) were adsorbed on the gold particle surfaces.

4.3 Structure and Photoelectrochemical Properties of Laminated Monoparticle Layers of CdS and ZnS on Gold

In a paper by T. Nakanishi, B. Ohtani and K. Uosaki of the Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Japan (*Jpn. J. Appl. Phys., Part 1*, 1999, **38**, 518-521) monolayers of CdS and ZnS nanoparticles are described and their layer-by-layer composite films were fabricated on a gold substrate that was pre-coated with a self-assembled monolayer (SAM) of 1,6-hexanedithiol. Semiconductor nanoparticles (*ca* 4 nm in diameter) were prepared in reversed micelles.

Evidence for the attachment of nanoparticles on SAM was obtained by XPS. A photoinduced anodic current was observed when the semiconductor nanoparticle electrodes were immersed in an electrolyte solution containing triethanolamine as the electron donor. The photocurrent action spectra of nanoparticle monolayers were in good agreement with the absorption spectra of nanoparticle dispersions before immobilization, indicating that the nanoparticles were immobilized on the substrate without changing their particle size. Layer-by-layer composite films of CdS and ZnS showed photoresponse depending on the order of accumulation. This indicates the successful fabrication of a layer-by-layer structure that affects the electron transfer through nanoparticles and the penetration of the electrolyte solution.

5 COLLOIDS AND NANOPARTICLES

5.1 Colloidal Gold Aerogels: Preparation, Properties, and Characterization

M.L. Anderson, C.A. Morris, R.M. Stroud, C.I. Merzbacher and D.R. Rolison of the Surface Chemistry Branch, Naval Research Laboratory, Washington, DC, USA (*Langmuir*, 1999, **15**, 674-681) have shown that colloidal metal aerogels are composite nanoscale materials that combine the high surface area and porosity of aerogels with the unique optical and physical properties of metal colloids. As such, they are being developed as advanced sensor, catalytic, and electrocatalytic materials. Colloidal gold-silica aerogels containing gold colloids ranging in size from 5 to 100nm have been prepared.

The results obtained focus on 5 and 28 nm gold-containing silica aerogels for the initial characterization of the interaction between the metal colloid and the silica matrix. A blue shift of the gold plasmon resonance for silica-immobilized gold colloids (relative to the same colloids in a native gold sol) indicates an interaction between the gold colloid and the nanoscale silica network.

TEM measurements were used to determine the average size and distribution of the colloidal gold particles, as well as to image the nanoscale silica environment supporting an immobilized gold colloid. Small-angle neutron scattering measurements show no significant changes in the three-dimensional structures of either the base- or acid-catalysed silica aerogels upon incorporation of small amounts (<0.1 vol%) of colloidal gold. However, for base-catalysed aerogels, nitrogen physisorption measurements reveal that the average pore size (relative to the pure silica aerogel) decreases as the size of the gold colloid is increased above the *ca* 10 nm domain size of the silica (which implies that the gold colloid occludes pore space) while it increases for 5 nm colloidal Au-silica aerogel. The accessibility of the gold surface in colloidal Au-silica aerogels to species introduced from solution is demonstrated by direct adsorption of the dye methyl orange to the gold surface.

5.2 Electrochemical Charge Injection into Immobilized Nanosized Gold Particle Ensembles: Potential Modulated Transmission and Reflectance Spectroscopy

Self-assembled multilayer thin films of nanometer-sized gold particles linked with organic dithiols have been prepared on glass, indium tin oxide, and gold substrates by T. Baum, D. Bethell, M. Brust and D.J. Schiffrin, Department of Chemistry, University of Liverpool, UK (*Langmuir*, 1999, **15**, 866-871). The gold particles within these structures retain their integrity and no sintering occurs as demonstrated by their optical absorbance, ellipsometry, and potential modulated transmission and reflectance spectroscopy. The optical response to electrochemical charge injection into the outermost layer of gold particles was found to be completely different from that of bulk gold electrodes, and it was concluded that the particles have to be regarded as discrete, immobilized quantum-dots.

5.3 Laser Photolysis Formation of Gold Colloids in Block Copolymer Micelles

L. Bronstein, D. Chernyshov, P. Valetsky, N. Tkachenko, H. Lemmetyinen, J. Hartmann and S.

Foerster of the Nesmeyanov Institute of Organoelement Compounds, Moscow (*Langmuir*, 1999, **15**, 83-91) have studied the laser photolysis of Au(III) salts embedded in micelle cores of block copolymer micelles derived from polystyrene-poly-4-vinylpyridine. Two types of polystyrene-poly-4-vinylpyridines having different block lengths were employed, producing micelles with different properties. Topics for study included the influence of the type of gold salt, loading rate, presence of water, micelle characteristics, and some other parameters on the rate of reduction and gold colloid formation. The presence of water in the system containing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was found to accelerate the Au(III) reduction, while the gold colloid size was not affected (*ca* 3 nm). The substitution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ with AuCl_3 results in much slower accumulation of AuI species, with subsequent slower nucleation of Au colloids, and this results in bigger particles with mean diameter of 6.0 nm. Increasing the amount of metal compound was found to increase the particle size.

5.4 Controlled Growth of Gold Nanoparticles During Ligand Exchange

Work demonstrating the feasibility of controlling core size of nanocrystals by variation of ligand has been described by L.O. Brown and J.E. Hutchison, Department of Chemistry and the Materials Science Institute, University of Oregon, Eugene, USA (*J. Am. Chem. Soc.*, 1999, **121**, 882-883). The ligand exchange between triphenylphosphine-stabilized gold nanoparticles (Au-TPP) and 1-pentadecylamine (PDA) produces amine-stabilized gold nanocrystals. The product nanocrystals (Au-PDA) show hexagonal packing assisted by a very narrow size distribution. Au-PDA forms deep red solutions exhibiting significant plasmon resonance ($\lambda_{\text{max}} = 525$ nm). In the solid state, thin films appear blue with a metallic reflectivity similar to that of plated gold (λ_{max} *ca* 590 nm). Further characterization of the material is performed with use of TEM, XPS, and NMR.

5.5 Preparation and Catalytic Effect of Gold Nanoparticles in Water

Stable gold nanoparticles of 2 nm diameter were prepared in water by chemical reduction of AuCl_4^- by NaBH_4 in the presence of CS_2 without adding any other stabilizers (K. Torigoe and K. Esumi, Department of Applied Chemistry, Institute of Colloid and Interface Science, Science University of Tokyo, Japan, *J. Phys. Chem. B*, 1999, **103**, 2862-2866). The

nanoparticles were proved by electron diffraction to be gold and not gold sulfides. In their UV-visible absorption spectra the surface plasmon (SP) band at around 520 nm is strongly damped, due to small particle size and possibly chemisorption of a CS_2 derivative. The time course of UV-vis reveals a rapid decrease of the 290 nm CT band of AuCl_4^- upon addition of CS_2 , suggesting their interaction before reduction of Au^{3+} . After the reduction of Au^{3+} has been completed, an intense band is built up at 330 nm which can be assigned to a reaction product of CS_2 and NaBH_4 . Furthermore, it was found that this reaction is promoted by gold nanoparticles, although no change was observed for the SP band intensity. This catalytic effect is also found with citrate-capped gold hydrosols.

6 ELECTROCHEMISTRY

6.1 Solution and Method for Electroless Plating of Gold

An Hitachi patent (H. Takehara, S. Ando, T. Inoue and T. Noguchi, Japanese Patent 11021672 A2 990126) describes the addition of anionic surfactant to displacement-type gold plating solutions consisting of gold complex ion, complexing agent, and pH controller, or to reduction-type gold plating solutions consisting of gold complex ion, complexing agent, pH controller, and reducing agent. Methods for the electroless plating of gold using the above solutions, and circuit substrates and electronic parts having gold plating, formed in the solutions, are also claimed. Plating of gold is carried out with high accuracy. The method is suitable for formation of gold wiring on substrates with high-density packaging.

6.2 Electrochemical Control of the Second Harmonic Generation Property of Self-Assembled Monolayers Containing a trans-Ferrocenyl-Nitrophenyl Ethylene Group on Gold

The second harmonic (SH) intensity at gold electrodes modified with self assembled monolayers (SAMs) of two novel molecules, which have trans-ferrocenyl-nitrophenyl ethylene and thiol groups as the second harmonic generation and surface-attached groups, respectively, is strongly dependent on the oxidation state of the ferrocene group (T. Kondo, S. Horiuchi, I. Yagi, S. Ye and K. Uosaki, Physical Chemistry Laboratory Division of Chemistry Graduate School of Science, Hokkaido University, Sapporo, Japan, *J. Am.*

Chem. Soc., 1999, **121**, 391-398). The SH intensity increased when the ferrocene moiety of the SAMs was oxidized electrochemically to the ferricenium cation, and it decreased and returned to the original value when the ferricenium cation of the ferrocene moiety was reduced to neutral ferrocene. These changes were reversible and were repeated many times. The molecular orientation change in each SAM upon reduction / oxidation of the ferrocene moiety was studied by *in situ* FTIR reflection-absorption spectroscopy, and the hyperpolarizabilities of these molecules were calculated using a computational electronic structure model. The origin of the SH intensity change is discussed.

6.3 Microbump Formation by Non-Cyanide Gold Electroplating

H. Watanabe, S. Hayashi and H. Honma of the Graduate School, Kanto Gakuin University, Yokohama, Japan (*J. Electrochem. Soc.*, 1999, **146**, 574-579) have described the formation of gold microbumps by electrodeposition using gold sulfite as a metal source. Gold bumps 20-80 μm wide and 20 μm high were fabricated by either direct or pulse current plating. Selection of additives in the plating bath is important for the formation of gold bumps having smooth surface without nodules.

Soft and uniform gold bumps can be obtained by adding 1-10 ppm of cerium ions in the plating bath. Removal of dissolved air in the plating solution is effective to avoid the skip plating and bubble pinholes on the bumps. Also, higher speed bump formation can be achieved by optimizing the pulse conditions, and the plating rate can be doubled compared with d.c. plating.

7 ELECTRONICS

7.1 Fibre Optic Sensor Based on Gold Island Plasmon Resonance

A fibre optic chemical sensor based on gold-island surface plasmon excitation has been developed by F. Merinudeau, T. Downey, A. Wig, A. Passian, M. Buncick and T.L. Ferrell, of LE2I, Le Creusot, France (*Sens. Actuators, B*, 1999, **B54**, 106-117). The sensing part of the fibre is a one inch portion on which cladding was removed and onto which a thin layer of gold was deposited to form a particulate surface. Annealing the gold reshapes the particles and produces an absorbance near 535 nm when the only medium residing outside the surface is air. A range of wavelengths provided by a white light source and monochromator is launched through the optical

fibre. The transmitted spectra display shifts in the resonance absorption due to changes in the medium surrounding, or adsorbed onto the fibre. Experimental results for the sensitivity and dynamic range in the measurement of solutions are in agreement with a basic theoretical model which characterizes the surface plasmon using non-retarded electrostatics. Also, the model assumes the particles are isolated oblate spheroids with a distribution of eccentricities.

7.2 Reliability and Process Characterization of Electroless Nickel-Gold/Solder Flip Chip Interconnect Technology

A paper by S. Wiegele, P. Thompson, R. Lee and E. Ramsland of the Semiconductor Products Sector, Motorola, Inc., Tempe, Arizona (*Proc. - Electron. Compon. Technol. Conf.*, 1998, **48**, 861-866) describes the reliability evaluation of the electroless Ni/Au solder interconnect technology under development in the Motorola Advanced Interconnect Systems Laboratory. This work was conducted jointly with the Motorola Automotive Products Division. The test vehicle used for evaluation is a high-power functional device which is assembled in a flip chip format to an organic test substrate using an epoxy material under an encapsulant. The reliability study evaluated the interconnect technology using both generic and application-specific reliability tests. Analysis of the reliability results and identification of failure mechanisms led to recommendations for process improvements. The Ni/Au solder interconnect has not failed after 1000+ cycles/h of reliability testing and has passed application-specific requirements for operational life.

8 MATERIALS SCIENCE

8.1 Layered Nanocomposite of Close-Packed Gold Nanoparticles and Titania Gel

T. Yonezawa, H. Matsune and T. Kunitake, Department of Chemistry and Biochemistry Graduate School of Engineering, Kyushu University, Japan (*Chem. Mater.*, 1999, **11**, 33-35) have described nanocomposites consisting of gold nanoparticles and TiO_2 ultrathin layers, prepared using a combination of layer-by-layer assembly and a surface sol-gel process. The gold nanoparticles stabilized by a monolayer of bis(11-hydroxyundecyl) disulfide were adsorbed on the surface of the TiO_2 gel and close-packed monoparticulate layers were formed. Multilayer films of TiO_2/Au nanoparticles were also prepared. The samples were characterized by SEM and UV-vis spectroscopy.

9 MEDICAL AND DENTISTRY

9.1 *Long-Term Urinary Platinum, Palladium, and Gold Excretion of Patients after Insertion of Noble-Metal Dental Alloys*

A study on the investigation of the extent to which noble-metal dental alloys contribute to the total Pt, Pd, and Au body burden of the general population has been reported by J. Begerow, J. Neuendorf, M. Turfeld, W. Raab and L. Dunemann, Department of Analytical Chemistry, Medical Institute of Environmental Hygiene, Duesseldorf, Germany (*Biomarkers*, 1999, **4**, 27-36). The urinary Pt, Pd, and Au excretion was determined in three non-occupationally exposed volunteers before and up to three months after insertion of a high-gold dental alloy. The *in-vitro* release of Pt, Pd, and Au from four different types of dental alloys into either artificial saliva or 1% lactic acid solution was also investigated. The Pt, Pd, and Au concentrations were determined by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS). Pt excretion levels remained high but the Au and Pd excretion in urine was not significantly increased after insertion of this type of high-gold dental alloy. The *in-vitro* investigations confirm the assumption that Pt, Pd, and Au are released from noble metal-containing dental alloys by corrosion. Under the applied conditions, the release was in the lower ng cm⁻² range. Thus, the Pt release from dental alloys can predominantly contribute to the Pt exposure of non-occupationally exposed persons. It can exceed the exposure from all other environmental sources including the Pt release from automobile exhaust catalysis.

10 METALLURGY

10.1 *Direct Atomistic Observation of Grain Boundary Sliding in Gold*

In this paper by T. Kizuka, M. Mizutani, S. Deguchi and M. Naruse, Department of Applied Physics, School of Engineering, Nagoya University, Japan [*Mater. Sci. Forum*, 1999, **304-306** (Towards Innovation in Superplasticity II), 555-559] grain boundary sliding in gold was caused at room temperature and directly observed inside a 200 kV high-resolution transmission electron microscope using a piezo-driving specimen holder. The grain in one side of the grain boundary was displaced at an atomic level along the boundary plane. The grain boundary sliding occurred *via* the displacement. The atomic process of the grain boundary sliding was observed *in situ* by time-resolved high-resolution TEM at a spatial resolution of 0.2 nm

and time resolution of 1/60 s. The so-called grain boundary sliding contained four elemental processes, *ie* (a) the sliding parallel to boundary plane, (b) the boundary migration perpendicular to boundary plane, (c) the variation in the direction of boundary plane, and (d) the rotation of crystallites beside the boundary.

11 REFINING

11.1 *Gold Leaching in an Alkaline Thiourea Solution*

Gold leaching with thiourea has been investigated in an alkaline solution by D. Wei, L. Chai, R. Ichino and M. Okido, Center for Integrated Research in Science and Engineering, Nagoya, Japan (*J. Electrochem. Soc.*, 1999, **146**(2), 559-563). In the presence of both Na₂SO₃ and Na₂S₂O₈, the chemical dissolution of gold can be accomplished in the alkaline thiourea solution. It was found that when used as a buffer, SO₃²⁻ can prevent thiourea from further decomposition into an insoluble species in contact with the oxidant S₂O₈²⁻ and that the mixed potential of gold is an important factor influencing thiourea decomposition and the rate of gold dissolution. Time dependence of the mixed potential and the dissolution mass for gold were also evaluated during the leaching process. This alkaline thiourea solution can be applied to gold extraction from gold resources containing silver, copper, nickel, and iron, because these metals normally do not dissolve in the solution.

11.2 *A Study of the Factors Affecting Copper Cementation of Gold from Ammoniacal Thiosulfate Solution*

E. Guerra and D.B. Dreisinger, Department of Metals and Materials Engineering, The University of British Columbia, Vancouver, Canada (*Hydrometallurgy*, 1999, **51**, 155-172) have studied how pH and ammonia, copper, thiosulfate and sulfite concentrations, and temperature, commonly manipulated in thiosulfate leaching studies, affect gold cementation performance using copper. These factors were varied in artificial leach solutions according to the ranges typically found in the literature. Both powder cementation and rotating disk electrode cementation were used to study the kinetics of gold cementation. Overall, the cementation of gold by copper from ammoniacal thiosulfate solution was under mass transfer control. Higher temperatures and pH/ammonia concentration increase the rate of gold cementation. Conversely, sulfite and copper in solution decrease cementation performance.