

Highlights from Recent Literature

Note:

A more comprehensive list of literature and patents, updated quarterly will be found in the searchable **Technical Database** on the World Gold Council website, www.gold.org under science and Industry domain.

1 Analytical

1.1 Gold Coating of Non-Conductive Membranes Before Matrix-Assisted Laser Desorption/Ionization Tandem Mass Spectrometric Analysis Prevents Charging Effect

Acquisition of tandem mass spectra from peptides or other analytes deposited on non-conductive membranes is inhibited on instruments combining matrix-assisted laser desorption/ionization with tandem time-of-flight analyzers (MALDI-TOF/TOF) due to a charging effect. A thin layer of gold renders the membrane conductive. A Scherl, C Zimmermann-Ivol, J Di Dio, A Vaezzadeh, P Binz, M Amez-Droz, R Cochard, J Sanchez; M Glueckmann, D Hochstrasser from the Biomedical Proteomics Research Group, Central Clinical Chemistry Laboratory, Geneva University Hospitals, Geneva, Switzerland, *Rapid Communications in Mass Spectrometry* 2005, **19(5)**, 605.

This allows adequate data acquisition on MALDI-TOF/TOF systems. Therefore, this methodology extends the capacity of the molecular scanner concept to tandem mass spectrometry.

1.2 Comparison of the Methods for Decomposition and Microwave-Assisted Closed Digestion of Hard Treated Compound for the Determination of Gold in $\text{KAu}(\text{CN})_2$

A novel microwave-assisted closed digestion method for decomposition of the difficultly treated compound of $\text{KAu}(\text{CN})_2$ was developed, and compared with the method of wet-heating, open-heating and oven-heating. L Zhu, E Zheng, Y Ma, Z An, from the Kunming Institute of Precious Metals, Kunming, Yunnan, 650221, Peoples Republic of China, *Guijinsu*, 2004, **25(3)**, 39. At the same time, the traditional gravimetric anal. was also compared with potentiometric titration under optimal conditions. Experimental results indicated that there was no significant differences between the microwave-assisted closed with other decomposition methods on the breaking of $\text{KAu}(\text{CN})_2$, and the accuracy (relative average error .ltoreq..+-.0.03%) and precision

(relative std. deviations .ltoreq. 0.02%) for gold analysis were almost the same. But the method of microwave-assisted closed digestion was more novel, rapid (30 min), economic and convenient one leading to widely apply.

1.3 Gold Nanoparticles with Different Capping Systems: an Electronic and Structural XAS Analysis

Gold nanoparticles (NPs) were prepared with three different capping systems: a tetralkylammonium salt, an alkanethiol, and a thiol-derivatized neoglycoconjugate. C Lopez-Cartes, T Rojas, R. Litran, D Martinez-Martinez, J De la Fuente, S Penades, A Fernandez from the Instituto de Ciencia de Materiales de Sevilla, and Grupo Carbohidratos, Laboratory of Glyconanotechnology IIQ, CSIC-Universidad Sevilla, Seville, Spain, *Journal of Physical Chemistry B* 2005, **109(18)**, 8761.

Also Au NPs supported on a porous TiO_2 substrate were studied. X-ray absorption spectroscopy (XAS) was used to determine the electronic behaviour of the different capped/supported systems regarding the electron/hole d. of d states.

Surface and size effects, as well as the role of the microstructure, were also studied through an exhaustive anal. of the EXAFS (extended x-ray absorption fine structure) data. Very small Gold NPs functionalized with thiol-derivatized mols. show an increase in d-hole d. at the Gold site due to Gold-S charge transfer. This effect is overcoming size effects (which lead to a slight increase of the d-electron d.) for high S:Gold at. ratios and core-shell microstructures where an atomically abrupt Gold-S interface likely does not exist. Also thiol functionalization of very small Gold NPs introduces a strong distortion as compared to fcc. order. To the contrary, electron transfer from reduced support oxides to Gold NPs can produce a higher increase in d-electron d. at the Gold site, as compared to naked Gold clusters.

1.4 Electron Holographic Characterization of Nano-Hetero Interface Effect in Gold Catalysts

The authors investigated the at. structure near the interface and the size dependence of the mean inner potential of gold in Au/TiO_2 catalysts prepared by the deposition precipitation (DP) method and the vacuum evaporation (VE) method using high resolution electron microscopy (HREM) and electron holography S Ichikawa, T Akita, K Okazaki, K Tanaka, M Kohyama, from the Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan, *Materials Research Society Symposium Proceedings*, 2005, Volume Date 2004, **839**. The TiO_2 supports prepared by DP method and VE method are considered to have oxygen-rich surfaces and titanium-rich surfaces respectively.

In case of the Au/TiO_2 catalyst prepared by DP method, the mean inner potential of gold increased depending on the size of the particle. When the size of the gold particle is over 5nm, the mean inner potential of gold was the same as that of bulk Gold. When the size is below 5nm, the mean inner potential

began to increase. It increases suddenly over 40V, particularly in case of below 2nm. It indicates that the electronic state of gold on TiO₂ changes from that of bulk state as the size decreases. On the other hand, the mean inner potential of gold in Au/TiO₂ catalysts prepared by VE method also increased as the size decreased, but the behaviour of the size dependence is different from that of DP method.

The critical size of the mean inner potential change is around 3nm. The size of the gold particle was below 3nm, the mean inner potential of gold increased gradually. The mean inner potential of VE method is less than that of DP method with the same particle size in spite of the size below 3nm. The stoichiometry at the interface between Gold and TiO₂ should be one of the dominant reasons for the behaviour difference of the size dependence of the mean inner potential between the preparations.

2 Catalysis

2.1 Preparation and Comparison of Supported Gold Nanocatalysts on Anatase, Brookite, Rutile, and P25 Polymorphs of TiO₂ for Catalytic Oxidation of CO

Nanosized anatase (.ltoreq.10 nm), rutile (.ltoreq.10 nm), and brookite (.apprx.70 nm) titania particles have been successfully synthesized via sonication and hydrothermal methods. W Yan, B Chen, S Mahurin, V Schwartz, D Mullins, A Lupini, S Pennycook, S Dai, S Overbury from the Chemical Sciences Division and Condensed Matter Physics Division, Oak Ridge National Laboratory, Oak Ridge, USA, *Journal of Physical Chemistry B*, 2005, **109(21)**, 10676. Gold was deposited with high dispersion onto the surfaces of anatase, rutile, brookite, and com. titania (P25) supports through a deposition-pptn. (D-P) process. All catalysts were exposed to an identical sequence of treatment and measurements of catalytic CO oxidation activity. The as-synthesized catalysts have high activity with concomitant Gold reduction upon exposure to the reactant stream. Mild reduction at 423 K produces comparably high activity catalysts for every support. Deactivation of the four catalysts was observed following a sequence of treatments at temps. up to 573 K. The brookite-supported gold catalyst sustains the highest catalytic activity after all treatments. XRD and TEM results indicate that the gold particles supported on brookite are smaller than those on the other supports following the reaction and pretreatment sequences.

2.2 Electrocatalytic Oxidation of Methanol: Carbon-Supported Gold-Platinum Nanoparticle Catalysts Prepared by Two-Phase Protocol

This paper describes recent results of a study of the electrocatalytic oxidation of MeOH at C-supported Gold and Au-Pt nanoparticle catalysts. J Luo, M Maye, N Kariuki, L Wang, P Njoki, Y Lin, M Schadt, R Naslund, C J Zhong from the

Department of Chemistry, State University of New York at Binghamton, Binghamton, USA, *Catalysis Today*, 2005, **99(3-4)**, 291. The exploration of the bimetallic compound on C black support is aimed at modifying the catalytic properties for MeOH oxidation reaction (MOR) at the anode in MeOH oxidation fuel cells. Gold and Gold-Pt nanoparticles of 2-3 nm core sizes with organic monolayer encapsulation were prepared by 2-phase protocol.

The nanoparticles were assembled on C black materials and thermally treated. The electrocatalytic MOR activities were characterized using voltammetric techniques, and were compared with common catalysts under several conditions. The results revealed some initial insights into the catalytic activity of Gold-Pt nanoparticle catalysts. Implications of the findings to the design and manipulation of highly-active Gold-Pt nanoparticle catalysts for fuel cell applications are also discussed.

2.3 Catalysis by Gold

A review; the recent interest in gold catalysis provides the focus for this perspectives paper. G Hutchings from the School of Chemistry, Cardiff University, Cardiff, UK, *Catalysis Today* 2005, **100(1-2)**, 55. Until recently gold has been overlooked as a key component of both homogeneous and heterogeneous catalysts. Two observations in the 1980s showed that gold could be a catalyst of choice, but it is only relatively recently that gold has been shown to be a very versatile redox catalyst. In this paper aspects of both the background to this interest and some of the recent work on gold will be discussed.

2.4 Gold Catalysts Supported on Fe- And Co-MCM-41

The ability of well-dispersed nanometric Gold particles on oxidic supports to catalyze the low-temperature oxidation of CO has attracted widespread research interest, particularly in pollution and automobile exhaust emission control. This work investigated the feasibility of coupling this property of Gold nanoparticles with the catalytically sought-for features of MCM-41 (high surface area and large pores) to improve the catalytic properties of gold for the near-ambient oxidation of CO. M Mokhonoana, N Coville, A Datye, from the Division of Chemistry, University of the North, Pietersburg, S. Africa, *Studies in Surface Science and Catalysis*, 2004, **154A**(Recent Advances in the Science and Technology of Zeolites and Related Materials), 827. Gold-containing. derivs. of MCM-41 were prepared both directly during synthesis, and post-synthetically using preformed MCM-41.

Large Gold particles resulted from the former method as a result of the high calcination temperatures needed to remove the template, whereas smaller particles were obtained in the latter method due to starting with an already ordered material, and using low activation temperatures. Pre-modification of MCM-41, with Fe or Co before the post-synthesis incorporation of Gold, improved the particle size distribution and the activity of the catalyst systems with

compatible metal contents. The Co-based systems showed better catalytic activity than their Fe-based counterparts for the same Gold content, a trend also observed for materials prepared by coprecipitation of the Gold and the Fe or Co precursor in the presence of calcined Si-MCM-41.

2.5 Gas-Phase Kinetics and Catalytic Reactions of Small Silver and Gold Clusters

A review; recent work on the chem. reactivity of mass-selected small silver and gold, as well as binary silver-gold cluster ions in a temperature controlled radio frequency ion trap arrangement is reviewed. T Bernhardt from the Institut für Experimentalphysik, Freie Universität Berlin, Germany, *International Journal of Mass Spectrometry* 2005, **243(1)**, 1. Reactions with molecular oxygen, carbon monoxide, and mixtures of both reactant gases are investigated, in order to reveal the possible role of these small noble metal cluster ions to act as gas-phase catalysts in the carbon monoxide combustion reaction. The obtained gas-phase reaction kinetics enable the detection of the reaction mechanisms as well as the energetics along the reaction pathway. A strong dependence of the chemical reactivity on cluster size, composition and charge state is found and correlations between electronic structure and reactivity are discussed in terms of simple frontier orbital pictures.

Special emphasis is put on the importance of cooperative adsorption effects on the small noble metal clusters. Through comparison of the kinetic data with first principles quantum chem. simulations, a comprehensive picture of the mol. details of the reaction behavior emerges. In particular, the experiments provide evidence that selected cluster ions act as active gas-phase catalysts for the oxidation of CO to CO₂ by molecular oxygen. In the case of Au₂⁻, the combination of reaction kinetics measurements with ab initio calculations even revealed the full and detailed reaction cycle of the catalytic gas-phase oxidation of CO.

2.6 CO Oxidation over Gold Nanocatalyst Confined in Mesoporous Silica

Gold nanoparticles embedded within mesoporous silica particles have been prepared and used as catalysts for CO oxidation. Y Chi, H Lin, C Mou from the Department of Chemistry and Center of Condensed Matter Science, National Taiwan University, Taiwan, *Applied Catalysis, A: General*, 2005, **284(1-2)**, 199. The silane APTS (H₂N(CH₂)₃-Si(OMe)₃) was used to surface-functionalize mesoporous silica in a direct method. The functionalized mesoporous silica was used to absorb the gold precursor AuCl₄⁻ and gold nanoparticles were formed inside the nanochannels after chem. reduction. The catalysts were activated by calcinations, followed with hydrogen reduction at 600 .degree.C. MCM-41, MCM-48 and SBA-15 were used as the supports to prepared Gold nanoparticles, resulting in different particle sizes of Gold. The catalysts are active in the oxidation of carbon monoxide, reaching activity values as high as 7.0 .times. 10⁻³ mmol g⁻¹ cat s⁻¹ at 353 K. The conversion of CO

increases with decreasing size of gold nanoparticles.

2.7 The Activity of Gold, Platinum, and Copper-Zinc Catalysts in the Oxidation of 1,2-Dichloropropane

The effect of supported Gold catalyst on oxidation of 1,2-dichloropropane (a waste byproduct in propylene oxide production by the chlorohydrin method) was studied and compared to the catalytic activity of alumina-supported Pt and Cu-Zn catalysts. M Kazmierczak, E Kaczmarek, A Zarczynski, T Maniecki from the Inst. Chem. Ogołnej i Ekol., Politech. Lodzka, Poland, *Przemysł Chemiczny*, 2005, **84(2)**, 114. The support, (K)Fe₂O₃, which was used for the Gold catalyst, was obtained by heating Fe(OH)₃ and Fe(NO₃)₃ with KOH, followed by calcination. The (K)Fe₂O₃ carrier alone, and (a) 1% Au/(K)Fe₂O₃ and, for comparison, (b) 0.06% Pt/(.gamma.)Al₂O₃, and (c) 27.3%Zn-27.8%Cu were used to catalyze for 8 h the oxidation of 32.5 g aq. 0.6 g/dm³ 1,2-dichloropropane per h with air at catalyst loads: (a) 64,500, (b) 10,000, and (c) 33,500 h⁻¹. The yields were (a) 99.4% (450.degree.C), (b) 98% (450.degree.C), and (c) 95% (475.degree.C), resp. Neither HCOH nor CO were formed, and the condensate contained 340mg Cl ions/dm³. The catalysts were stable and active in the descending order a > b > c.

2.8 Aerobic Oxidation of Cyclohexane by Gold Nanoparticles Immobilized upon Mesoporous Silica

A series of highly efficient hybrid gold nanoparticle/mesoporous-silica catalysts were synthesized and employed for the solvent-free aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone under moderate reaction conditions. K Zhu, J Hu, R Richards from the International University Bremen, Germany, *Catalysis Letters*, 2005, **100(3-4)**, 195. The catalysts were characterized by XRD, N₂ adsorption/desorption, TEM and ICP-AES, which shows the active species are monodispersed gold nanoparticles.

2.9 Effect of the Preparation of Supported Gold Particles on the Catalytic Activity in CO Oxidation Reaction

Gold catalysts supported on hydrotalcite (HT) with a Mg:Al molar ratio 4:2 were prepared by direct anionic exchange (DAE) or by deposition-precipitation (DP) with NaOH or urea, in order to investigate the influence of the synthesis parameters on the catalytic conversion in CO oxidation. The highest activity was obtained for Au/Mg⁴Al² prepared by DAE. I Dobrosz, K Jiratova, V Pitchon, J Rynkowski from the Institute of Chemical and Ecological Chemistry, Technical University of Lodz, Poland, *Journal of Molecular Catalysis A: Chemical*, 2005, **234(1-2)**, 187. The influence of various parameters on CO conversion such as the HAuCl₄ concentration in the initial solution, the washing procedure, the pre-treatment temperature, the precursor of HT and the gold loadings were investigated. This study confirms the poisoning effect of chloride.

The average gold particle size is higher for the catalysts with higher residual chloride content. In order to remove the remaining chloride from the sample, different washing procedures were used, i.e. either with warm water or with ammonia. Changes in activity and particle size were observed according to the washing procedure. Higher calcination temperature increases the surface area of HT, contributing to better dispersion of gold. A smaller particle size, as measured by XRD and TEM, is obtained on HT prepared from sulfate precursor rather than nitrate.

3 Chemistry

3.1 Formation of Molecularly Chemisorbed Oxygen On TiO₂-Supported Gold Nanoclusters and Au(111) from Exposure to an Oxygen Plasma Jet

The authors present results of a study into the low-temperature formation of molecularly chemisorbed oxygen on a Au/TiO₂ model catalyst and on a Au(111) single crystal during exposure to a plasma jet of oxygen. J Stiehl, T Kim, S McClure, C Mullins from the Department of Chemical Engineering and Texas Materials Institute, The University of Texas at Austin, USA, *Journal of Physical Chemistry B*, 2005, **109(13)**, 6316. Through the use of collision-induced desorption measurements and isotopic mixing expts. the authors show evidence suggesting that at least some of the molecular oxygen is formed as a result of recombination of oxygen atoms on the samples during the plasma exposure. Of course, adsorption of excited mol. oxygen directly from the gas phase may also take place. The authors also present evidence showing that the adsorption of oxygen atoms on the surface assists in the mol. chemisorption of oxygen on the Au/TiO₂ model catalyst samples. Thus, oxygen molecules impinging on the samples during plasma-jet exposures (plasma jet has .apprx.40% dissociation fraction) could have an enhanced probability of adsorption due to simultaneous oxygen atom adsorption.

3.2 Synthesis and Reactivity of Dimethyl Gold Complexes Supported on MgO: Characterization by Infrared and X-ray Absorption Spectroscopies

Di-Me Au complexes bonded to partially dehydroxylated MgO powder calcined at 673 K were synthesized by adsorption of AuMe₂(acac) (acac is C⁵H⁷O²) from n-pentane solution. J Guzman, B Anderson, C Vinod, K Ramesh, J Niemantsverdriet, B Gates from the Department of Chemical Engineering and Materials Science, University of California, Davis, CA, USA, *Langmuir*, 2005, **21(8)**, 3675. The synthesis and subsequent decomposition of the complexes by treatment in He or H₂ were characterized with diffuse reflectance FTIR (DRIFT), x-ray absorption near edge structure (XANES), and extended x-ray absorption fine structure (EXAFS) spectroscopies.

The XANES results identify Au(III) in the supported

complexes, and the EXAFS and DRIFTS data indicate mononuclear di-Me Au complexes as the predominant surface Au species, consistent with the lack of Au-Au contributions in the EXAFS spectrum and the presence of .nu.asMe and .nu.sMe bands in the IR spectrum. EXAFS data show that each complex is bonded to two O atoms of the MgO surface at an Au-O distance of 2.16 .ANG.. The DRIFT spectra show that reaction of AuMe₂(acac) with MgO at room temperature also formed Mg(acac)₂ and H(acac) species on the support. Treatment of the di-Me Au complexes in He or H₂ at increasing temps. = 373-573 K removed CH₃ ligands and caused aggregation forming zerovalent Gold nanoclusters of increasing size, ultimately with an av. diameter of .apprx.30 .ANG.. Anal. of the gas-phase products during the genesis of the Gold clusters indicated formation of CH₄ (consistent with removal of CH₃ groups) and CO₂ at 473-573 K, associated with decomposition of the org. ligands derived from acac species. O₂ and CO₂ were also formed in the decomposition of ubiquitous carbonates present on the surface of the MgO support.

3.3 Interaction of Ozone with Gold Nanoparticles

Gold nanoparticles interact with aqueous ozone to produce a surface plasmon resonance shift without aggregation of the nanoparticles. Given ozone's destructive nature, the surprising finding was that the Gold nanoparticles returned to their original color and were able to cycle between the wavelengths as ozone was introduced and removed. Gold islands were made and tested for a gaseous ozone response. S Puckett, J Heuser, J Keith, W Spendel, G Pacey from the Miami University Center for Nanotechnology, Department of Chemistry and Biochemistry, Miami University, USA, *Talanta*, 2005, **66(5)**, 1242. Similarly to the aqueous system, the Gold islands show a cycling effect. Potentially, this system would be useful as a sensor that identifies the presence of ozone in gaseous media.

3.4 A Surface Adsorption/Reaction Mechanism for Gold Oxidation By Copper(II) in Ammoniacal Thiosulfate Solutions

Literature data for Gold dissolution in ammoniacal Cu(II) thiosulfate solutions is reinterpreted from adsorption and mixed potential theory. The dissolution reaction appears to take place via the adsorption of Cu(II)-NH₃⁻ thiosulfate onto the Gold surface, forming the adsorbed species |-Au(S₂O₃)_nCu(NH₃)_{-(2n-2)}p. G Senanayake from the Department of Extractive Metallurgy and Mineral Science, Murdoch University, Perth, Australia, *Journal of Colloid and Interface Science*, 2005, **286(1)**, 253. Equil. constants for the formation of these species from Cu(NH₃)₂+m are in the range K_{ads} = 172-510 (molar units) for m = 4, n = 1 or 2, and p = 2 or 3. These complexes decompose with a rate const. of k_{Au} = 1.7 .times. 10⁻⁴ molm-2s⁻¹, to produce Au(S₂O₃)³⁻² and Cu(NH₃)₃⁺ or Cu(NH₃)₂⁺, where the Cu(I) complexes in solution are reequilibrated to the more stable species Cu(S₂O₃)⁵⁻³.

3.5 Iron Oxide-Gold Core-Shell Nanoparticles and Thin Film Assembly

This paper reports findings of an investigation of the synthesis of monolayer-capped iron oxide and core (iron oxide)-shell (gold) nanocomposite and their assembly towards thin film materials. L Wang, J Luo, M Maye, Q Fan, Q Rendeng, M Engelhard, C Wang, Y Lin, C J Zhong from the Department of Chemistry, State University of New York at Binghamton, Binghamton, NY, USA, *Journal of Materials Chemistry*, 2005, **15(18)**, 1821. Pre-synthesized and size-defined iron oxide nanoparticles were used as seeding materials for the reduction of gold precursors, which was shown to be effective for coating the iron oxide cores with gold shells (Fe oxide@Au). The unique aspect of their synthesis is the formation of Fe oxide@Au core-shell nanoparticles with controllable surface properties. The novelty of their assembly strategy is the exploitation of the ligand-exchange reactivity at the gold shells for the thin film assembly of the core-shell nanoparticles. The core-shell nanocomposites and assemblies have been characterized using TEM, XRD, XPS, FTIR, TGA, and DCP-AES techniques. In addition to evidence from TEM detection of the change in particle size, UV-Vis observation of the change in the surface plasmon resonance band, and XRD detection of disappearance of the magnetite diffraction peaks after coating the gold shell, the formation of the core-shell morphol. was further confirmed by DCP-AES compn. anal. of Gold and Fe in the molecularly-mediated thin film assembly of Fe oxide@Au particles.

The interparticle ligand exchange-pptn. chem. at the gold shell is to their knowledge the first example demonstrating the inter-shell reactivity for constructing thin films of Fe oxide@Au particles. The authors suggest that the results have provided important insights into the design of interfacial reactivities via core-shell nanocomposites for magnetic, catalytic and biol. applications.

4 Electrochemistry

4.1 Electrochemistry on Alternate Structures of Gold Nanoparticles and Ferrocene-Tethered Polyamidoamine Dendrimers

Self-assembled systems with polyamidoamine (PAMAM) dendrimers combined with gold nanoparticles were studied for potential applications in mol. electronics, catalyst carriers, chem. sensors, and biomedical devices. J Suk, J Lee, J Kwak from the Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), S. Korea, *Bulletin of the Korean Chemical Society*, 2004, **25(11)**, 1681. Gold nanoparticle monolayers and multilayers with pure and ferrocene-tethered PAMAM dendrimers were deposited on a mixed self-assembled monolayer. The various generations of PAMAM dendrimers can be covalently attached to mercaptoundecanoic acid mixed with a mercaptoundecanol self-assembled monolayer. Cyclic voltammograms show that

redox peak current on the alternate multilayers of gold nanoparticles and ferrocene-tethered PAMAM dendrimers increase as the no. of layers increases. Fourier transform IR external reflection spectroscopy and SEM support the results from electrochemical measurements.

4.2 Electrochemical Deposition of Copper on Polycrystalline Gold from Thiocyanate Solutions

The initial stages of copper electrodeposition on to a polycrystalline gold electrode from a solution contg. 0.05 M Cu (I) and 3 M KSCN were studied by cyclic voltammetry and potentiostatic step techniques. D Simkunaite, E Ivaskevici, I Valsiunas A Steponavicius from the Institute of Chemistry, Vilnius, Lithuania, *Bulletin of Electrochemistry*, 2004, **20(8)**, 371. The composition of the copper thiocyanate solution was also detected. Some comments on the characterization of the gold surface in a thiocyanate medium are made. It was established that at potentials more neg. than the equil. potential for the couple Cu/Cu^+ , SCN^- , the initial stages of the deposition occurred through progressive a 3-dimensional nucleation and growth under a diffusion control model developed by Scharifker and Hills. From the chronoamperometric data, the experimental values of the diffusion coeff. of Cu (I)-thiocyanate complex and the stationary nucleation rate I_{st} at a specific copper deposition potential were detected

5 Electronics and Sensors

5.1 Manufacturing of Nanoscale Thickness Gold Lines by Laser Curing of a Discretely Deposited Nanoparticle Suspension

The present work is focused on a novel method for the manufacturing of elec. microconductors for semiconductors and other devices. N Bieri, J Chung, D Poulikakos, C Grigoropoulos from the ETH Center, Institute of Energy Technology, Laboratory of Thermodynamics in Emerging Technologies, Swiss Federal Institute of Technology, Zurich, Switzerland, *Superlattices and Microstructures*, 2004, **35(3-6)**, 437. Three different technologies are combined in this technique: controlled (drop on demand) printing, laser curing, and the employment of nanoparticles of matter, possessing markedly different properties (here, m.p.) than their bulk counterparts. A modified on demand ink jet process was used to print elec. conducting line patterns from a suspension of Gold nanoparticles in toluene. Microdroplets of 60-100 . μm diameter are generated and deposited on a moving substrate such that the droplets form continuous lines. Focused laser irradiation was used to evaporate the solvent, melt the metal nanoparticles in the suspension, and sinter the suspended particles to form continuous, elec. conducting Gold microlines on a substrate. The ultrafine particles in the suspension have a diameter size range of 2-5 nm. Due to curvature and surface effects of such small

particles, the m.p. is markedly lower than that of bulk Gold (1063 C). At. force microscopy and SEM were employed to study the topol. of the cured line. In situ visualization of the curing process was conducted. Results on the effect of the laser irradsn. power on the topol. and width of the cured line, which is directly related to the elec. cond., are reported.

5.2 Construction of Pegylated Gold Colloid-Assembled Surface for High Performance Biosensor

Heterotelechelic poly (ethylene glycol) possessing an acetal group at one end and a mercapto group at the other chain end (acetal-PEG-SH) was prepared by an original synthetic route. T Ishii, Y Suzuki, Y Akiyama, H Otsuka, K Kataoka, Y Nagasaki from the Department of Material Science and Technology, Tokyo University of Science, Yamazaki, Noda, Japan, *Kobunshi Ronbunshu*, 2005, **62(2)**, 81. Using the acetal-PEG-SH, we carried out a modification of gold colloid to improve its dispersion stability as well as the non-fouling character of its surface.

The acetal-PEG gold colloid thus obtained was treated with hydrochloric acid to convert the acetal group into an aldehyde group; then it was treated by a primary amino group via a reductive amination reaction with ammonia. The obtained amino-PEGylated gold colloids showed high dispersion stability under the physiol. conditions. The amino-PEGylated gold colloid was fixed on the surface plasmon sensor surface via covalent linkage using a NHS-linker.

The amine-PEG-gold colloid surface prevented the protein nonspecific adsorption due to the PEG brush on the colloid surface. In addition, the sensitivity as SPR sensor increased significantly. Actually, 0.1 mg/mL biotin deriv. can be effectively detected on the PEGylated gold colloid-modified surface, indicating that the PEGylated gold colloids-modified SPR sensor chip contributed to the enhancement of the SPR sensitivity.

5.3 Development of Air Stable Polymer Solar Cells Using an Inverted Gold on Top Anode Structure

The authors developed indium-tin-oxide/perylene diimide (or bathocuproine (BCP))/poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and [6,6]-Ph C60 butyric acid Me ester (PCBM) blend/copper phthalocyanine (CuPc)/Au interpenetrated network polymer solar cells to improve air stability. Y Sahin, S Alem, R de Bettignies, J Nunzi from the Equipe de Recherche Technologique Cellules Solaires Photovoltaïques Plastiques, Propriétés Optiques des Matériaux et Applications, Laboratoire associé au Centre National de la Recherche Scientifique 6136, Université d'Angers, France, *Thin Solid Films*, 2005, **476(2)**, 340. The stability properties of the cells were characterized by current-voltage measurements under the influence of light and air. The authors achieved long lifetime solar cells which work at least 2 wk under ambient air conditions without encapsulation. Solar energy conversion efficiency of the cells

decrease 30% of the 1st day value at the end of 2 wk. Photocurrent absorption properties of the devices were also studied.

5.4 Pairs of Gold Electrodes with Nanometer Separation Performed Over SiO₂ Substrates With a Molecular Adhesion Monolayer

Pairs of electrodes with nanometer separation (nano-gap) are achieved through an electromigration-induced break-junction (EIBJ) technique at room temperature. Lithog. defined gold (Au) wires are formed by e-beam evapn. over oxide coated silicon substrates silanized with (3-Mercaptopropyl)trimethoxysilane (MPTMS) and then subjected to electromigration at room temperature to create a nanometer scale gap between the two newly formed Gold electrodes.

A Mahapatro, S Ghosh, D Janes from the School of Electrical and Computer Engineering, Purdue University, West Lafayette, USA, *Los Alamos National Laboratory, Preprint Archive, Condensed Matter*, 2005, **1**. The Si-O-Si covalent bond at the SiO₂ surface and the Gold-sulfur (Au-S) bond at the top evapd. Gold side, makes MPTMS as an efficient adhesive monolayer between SiO₂ and Gold. Although the Gold wires are initially 2.μm wide, gaps with length .apprx.1nm and width .apprx.5nm are observed after breaking and imaging through a field effect scanning electron microscope (FESEM).

This technique eliminates the presence of any residual metal interlink in the adhesion layer (chromium or titanium for Gold deposition over SiO₂) after breaking the gold wire and it is much easier to implement than the commonly used low temperature EIBJ technique which needs to be executed at 4.2 K. Metal-mol.-metal structures with sym. metal-mol. contacts at both ends of the mol., are fabricated by forming a self-assembled monolayer of -dithiol mols. between the EIBJ created Gold electrodes with nanometer separation. Elec. conduction through single mols. of 1,4-Benzenedimethanethiol (XYL) is tested using the Au/XYL/Au structure with chemisorbed gold-sulfur (Au-S) coupling at both contacts.

5.5 A Multi-Stack Insulator Silicon-Organic Memory Device with Gold Nanoparticles

The authors demonstrate a memory device using Gold nanoparticles as charge storage elements deposited at room temperature by chem. processing. S Kolliopoulou, D Tsoukalas, P Dimitrakis, P Normand, H Zhang, N Cant, S Evans S Paul, C Pearson, A Molloy, M Petty from the Institute of Microelectronics, NCSR Demokritos, Aghia Paraskevi, Greece, *ESSDERC 2003, Proceedings of the European Solid-State Device Research Conference, 33rd, Estoril, Portugal, Sept. 16-18, 2003*, 477.

The nanoparticles are deposited over a thin thermal SiO₂ layer that insulates them from the device Si channel. An org. insulator deposited by the Langmuir-Blodgett technique at room temperature separates the Al gate electrode from the

nanoparticles. The device exhibits significant threshold voltage shifts after application of low voltage pulses (± 7 V) to the gate and has nonvolatile retention time characteristics.

5.6 Packaging of Copper/Low-K IC Devices: A Novel Direct Fine Pitch Gold Wirebond Ball Interconnects onto Copper/Low-K Terminal Pads

The trend toward finer pitch and higher performance devices has driven the semiconductor industry to incorporate copper and low-k dielec. materials. Compared to the commonly used aluminum metalization scheme on the traditional silicon dioxide and/or silicon nitride passivation, a Cu/low-k combination offers higher on-chip communication speed and a lower overall device cost.

However, the process of packaging Cu/low-k devices has been proven to be difficult, relying either on addnl. lithog. and deposition steps or on costly new process tools. Thus, this paper presents a novel methodol. to bond fine pitch Gold wire directly onto the Cu/low-k pad structure using the industry std. tool set. S Chungpaiboonpatana, F Shi from the Department of Chemical Engineering and Material Science, Henry Samueli School of Engineering, University of California, USA, *IEEE Transactions on Advanced Packaging*, 2004, **27(3)**, 476. A Cu/low-k test vehicle is designed with the required slotted low-k fillings for dual damascene chem. mech. polishing (CMP) process need. In addition, a thin org. passivation film is developed for coating the exposed Cu/low-k pad temporarily from copper oxidation and to provide a wirebondable surface to form the proper interconnects. A design of expt. is performed to optimize wirebonding parameters (power, time, and ultrasonic gauge (USG) bleed), along with key phys. contributors from wafer sawing and die attaching steps that impact the interconnect shear strength and quality. In addition, elec. and optical characterization and surface failure anal. are performed to confirm the feasibility of the technology Finally, reliability results of the pad structure design and recommendations for further process optimization are presented.

5.7 The Future of Gold in Electronics

A review. Gold-based materials were a mainstay of the electronics and semiconductor industry since the physics was just a lab. curiosity. Gold is the workhorse material in wire bond, flip chip and off wafer interconnections due to its corrosion resistance, ability to form metallurgical bonds by soldering or cold welding, and ease of fabrication. T Ellis from Triaxial Structures Inc., Philadelphia, USA, *Gold Bulletin (London, United Kingdom)* 2004, **37(1-2)**, 66. As the electronics and semiconductor industries grew, so did the use of gold in spite of the feature size reduction so elegantly demonstrated in Moore's law.

However, several revolutions in the Silicon miracle are threatening gold's place as the material of choice. Although

cost is always an issue, the limitations are assocd. with the chem. of gold based alloys. Will gold remain. Emerging requirements of bioelectronics, photonics and power requirements in conventional device represent new opportunities for gold to shine. Additionally, as the world market demand for electronic, semiconducting, bio-electronic and photonic technology increases, given the right technology, gold still can provide value proposition.

6 Medical and Dental

6.1 Effect of Gold Coating on Interfacial Reaction Between Dental Porcelain And Titanium

Cross-sectional microstructure observation of the titanium firing porcelain inserted ion-coated gold layer was performed by SEM-EDX that can analyze light elements from boron. Two gold-coated samples applied to mirror finished titanium surface were prepared; one was applied only degassing treatment, and the other was applied firing after degassing treatment. E Miura, T Tabaru, J Liu, Y Tanaka, T Shiraishi, K Hisatsune from the Department of Developmental and Reconstructive Medicine, Course of Medical and Dental Sciences, Graduate School of Biomedical Sciences, Nagasaki University, Nagasaki, Japan, *Materials Transactions*, 2004, **45(10)**, 3044. In addition, in order to investigate effect of the gold coating, titanium/porcelain samples without coating were also observed. From SEM-EDX observation of the specimen, approx. 2.5 μm thickness titanium oxide layer appeared across the gold film in the first sample.

In the titanium firing porcelain after degassing treatment, two obvious reaction layers appeared across the gold coating.

One included mainly titanium and oxygen, and another included titanium, gold and aluminum. Thickness of the reaction layers was approx. 2.5-3 μm . From the results, it is suggested titanium was diffused into porcelain through a gold coating, and titanium oxide was formed at an interface. Titanium/porcelain without gold coating had two reaction layers at the interface, however, many cracks and crevices were exhibited in the layer and between the layers. Effect of gold coating on interfacial layer formation was discussed by the comparison with titanium/porcelain interface without gold coating. Thickness of the reaction layers decreased by gold coating, and cracks and crevices in the layer disappeared.

The results suggested that oxygen diffusion became lower due to existence of the coating, and titanium-gold reaction changed layer's microstructure. It is also suggested that gold diffusion into the reaction layer and restriction of oxygen diffusion contribute to the reaction layer formation, consequently gold coating on titanium substrate contributes to improvement of adhesion between titanium and porcelain.

6.2 The Surface Free Energy of Dental Gold-Based Materials

A gold composite material (Captek) has been developed which is claimed to resist plaque deposition. This study's aim was to compare the surface free energy (SFE) of this composite material with that of a type III casting gold. S Knorr, E Combe, L Wolff, J Hodges from the Minnesota Dental Research Center for Biomaterials and Biomechanics, School of Dentistry, University of Minnesota, Minneapolis, USA, *Dental Materials*, 2005, **21(3)**, 272. Contact angle measurements, using the Wilhelmy technique, were made on four bar-shaped samples of each material, using five test liqs. (diiodomethane, ethylene glycol, formamide, glycerol and water) and four measurements per sample per liquid. For each material, the dispersive, Lewis acid and Lewis base components of SFE (γ_{DS} , γ_{+S} , γ_{-S} , resp.) were estd. by least squares anal. and also by a Bayesian method. The gold composite material and the type III casting gold did not differ significantly in their γ_{DS} values (95% confidence interval for gold composite minus type III gold, -5.0 to +2.7). Both materials had low γ_{+S} values in common with most solids. The gold composite had a significantly lower Lewis base component of SFE than the type III gold-8.4 mN/m for the former material compared to 19.1 mN/m for the latter (95% confidence interval for gold composite minus type III gold, -16.4 to -4.9). The difference between materials could be related to the lack of non-precious metals and the structure of the gold composite material. It is hypothesized that difference in γ_{-S} components of SFE may be an important parameter in predicting bacterial adhesion and plaque resistance. Methods that only det. SFE as a single parameter may be unable to differentiate adequately between dental restorative materials.

7 Metallurgy, Materials and Coatings

7.1 Adherence of Self-Assembled Monolayers on Gold and Their Effects for High-Performance Anisotropic Conductive Adhesives

To improve the elec. property of the anisotropic conductive adhesive (ACA) joints, self-assembled monolayer (SAM) compounds are introduced into the interface between the metal filler and the substrate bond pad. Y Li, K Moon, C Wong from the School of Materials Science and Engineering and Packaging Research Center, Georgia Institute of Technology, Atlanta, USA, *Journal of Electronic Materials* 2005, **34(3)**, 266. The formation of the SAM on gold and the thermal stability were investigated by measuring the contact angles of SAM compounds with a hydrophilic or hydrophobic tail groups such as octadecanethiol (ODT), mercaptoacetic acid (MAA), and 1,4-benzenedithiol (dithiol) on the Gold surface. Epoxy resins with two different curing temps. were used as polymer matrixes of the ACA formulations. The SAM-treated ACA joints showed much

lower resistance at the same applied current than nontreated joints, and the effect on the low curing temperature epoxy matrixes was more significant.

7.2 Measurement of the Mechanical Properties of Electroplated Gold Thin Films Using Micromachined Beam Structures

The authors have measured the Young's modulus, residual stress, and stress gradient of electroplated gold thin films using surface micromachined beam structures. C Baek, Y Kim, Y Ahn, Y Kim from the School of Electrical Engineering and Computer Science, Seoul National University, Seoul, S. Korea, *Sensors and Actuators, A: Physical*, 2005, **A117(1)**, 17. Cantilever and bridge beam structures of different lengths were fabricated using UV-LIGA surface micromachining and dry-release methods.

The Young's modulus and residual stress of the fabricated beams were detected from the resonance frequencies of electrostatically excited beams, and the stress gradient was evaluated from the self-deformation of released cantilevers. The observed Young's modulus was smaller than the bulk Young's modulus, and showed small changes depending on the deposition c.d.

The av. residual stress was found to be tensile in nature, and the observed residual stresses showed no differences, regardless of the c.d. However, the stress gradient increased with increasing c.d. The deformation of the cantilever beam after release was dependent on the plasma ashing time used. This result implies that additional thermal effects from the post-deposition process may have an influence on the final performance of fabricated micro electro mech. systems (MEMS) devices.

7.3 Effect of Copper, Silver and Gold on Tensile Behaviour in Al-Mg-Si Alloy

It is very popular to improve mech. properties of Al-Mg-Si alloys by adding other element. For example, it is well known that addition of transition metals is useful because the refinement of grain size can be achieved, and with the addition of Cu to Al-Mg-Si alloy can increase the strength and hardness of the materials. Also, there are a few reports about the addition of Ag and Au, which is particularly good for elongation. However, even now it is not clarified why Cu, Ag and Au are useful in improving alloys elongation.

The authors have investigated the tensile behavior of 2 types of Al-Mg-Si alloy, namely balanced alloy and excess Si alloy, which both contain Cu, Ag and Au. K Matsuda, K Fukaya, Z Young, T Kawabata, Y Uetani, S Ikeno from the Faculty of Engineering, Toyama University, Toyama, Japan, *Materials Forum* 2004, **28**, 424. The tensile test and hardness measurement were carried out. Microstructures of the matrix and the grain boundary were observed with TEM, and SEM was used to investigate the fracture surfaces. Elongation of the alloys bearing Cu, Ag and Au were essentially improved, and the width of the ppt. free zone was found to be wider than alloys without those 3 elements.

8 Nanotechnology

8.1 Gold Nanoparticle Formation from Photochemical Reduction of Au³⁺ by Continuous Excitation in Colloidal Solutions. A Proposed Molecular Mechanism

A photochemical reduction of Au³⁺ with continuous 250-400 nm excitation is studied in ethylene glycol, and poly(vinylpyrrolidone) (PVP) is used as a capping material. After the absorption of Au³⁺ disappears, excitation is stopped. The surface plasmon absorption of gold as well as the thermal reappearance of the Au³⁺ absorption are found to increase as a function of time. S Eustis, H Hsu, M El-Sayed from the Laser Dynamics Laboratory, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, USA, *Journal of Physical Chemistry B*, 2005, **109(11)**, 4811. The rates of these changes are studied as a function of the mole fraction of ethylene glycol in water.

Experimental results show that a small amt. of ethylene glycol increases the formation of gold nanoparticles and decreases the reformation of the Au³⁺ absorption after irradiation. Increasing the glycol concentration first increases the rate of formation of gold nanoparticles to a max. at a mole fraction 0.40. As the glycol concentration is further increased, the rate of formation of the gold nanoparticles and the rate of reformation of Au³⁺ decrease. A mechanism is proposed that involves the reduction of the excited Au³⁺ to Au²⁺ by ethylene glycol. This is followed by the disproportionation of Au²⁺ to Au³⁺ and Au¹⁺. Both the reduction of Au¹⁺ by ethylene glycol and its disproportionation lead to the formation of Au⁰, which upon nucleation and growth form Au.

8.2 Formation of Gold Nanoparticles by Good's Buffers

Gold nanoparticle formation was found from tetrachloroaurate(III) in the presence of Good's Buffers, such as 2-morpholinoethanesulfonic acid (MES) and 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES), which are used widely in labs. for studies of anal., inorg., phys., and bio-chem. as well as biol. A Habib, M Tabata, G Wu from the Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga, Japan, *Bulletin of the Chemical Society of Japan*, 2005, **78(2)**, 262.

The obtained gold nanoparticles were examined by UV-Visible Spectroscopy (UV-vis), Dynamic Light Scattering (DLS) and Electrophoretic Light Scattering (ELS) in an aq. system and by transmission electron microscopy (TEM) for particle morphologies. UV-vis spectra showed absorption maxima at .apprx.530 and .apprx.750 nm, depending on the buffer reagents and their concentration, pH, and ionic strength. The size and the surface zeta potential of the formed nanoparticles were 23 to 73 nm and -30 to -12 mV, resp. The TEM pictures clearly indicated the formation of finely dispersed, chained, or aggregated gold nanoparticles, depending on the experimental conditions.

The mechanism of gold nanoparticle formation was studied by the measurements of cyclic voltammetry (CV) and ESR (ESR). MES and HEPES showed a pos. anodic peak at approx. +800 mV vs Ag/AgCl electrode, which indicated that these buffering agents have mild reducing ability. ESR results indicated the generation of nitrogen-centered cationic free radicals from these Good's Buffers in the presence of Au(III), resulting in the formation of gold nanoparticles. A reaction mechanism is proposed.

8.3 Polymer-Stabilized Colloidal Gold: A Convenient Method for the Synthesis of Nanoparticles by a UV-Irradiation Approach

A simple and convenient photochemical method for the preparation of polymer-stabilized colloidal gold by using UV irradiation is described. K Mallick, M Witcomb, M Scurrall from the Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Wits, S. Africa, *Applied Physics A: Materials Science and Processing* 2004, Volume Date 2005, **A80(2)**, 395. Methoxy polyethylene glycol acts as the reducing agent in the presence of the UV irradiation towards gold ions and also acts as the stabilizer of the gold nanoparticles. The gradual broadening of the UV-visible spectra of the stabilized gold system reflects the formation of larger particles with a longer period of exposure to the UV radiation.

8.4 Continuous Synthesis of Gold Nanoparticles in a Microreactor

A continuous flow microreactor was used for the synthesis of gold nanoparticles (5 to 50 nm) directly from a gold salt (HAuCl₄) and a reducing agent (ascorbic acid). J Wagner J Koehler from the Physical Chemistry and Microreaction Technology, Department Institute of Physics, Technical University of Ilmenau, Germany, *Nano Letters*, 2005, **5(4)**, 685. Experimental parameters were optimized to obtain narrow size distributions, which were at av. two times narrower than those obtained in a conventional synthesis. Addnl., two approaches, i.e., elevation of pH during reaction and hydrophobization of internal reactor surfaces were tested to suppress reactor fouling.

8.5 Solidification of Gold Nanoparticles in Carbon Nanotubes

The structure and the solidification of Gold nanoparticles in a C nanotube were studied using mol. dynamics simulations. S Arcidiacono J Walther, D Poulikakos, D Passerone, P Koumoutsakos from the Laboratory of Thermodynamics in Emerging Technologies, ETH, Zurich, Switzerland, *Physical Review Letters* 2005, **94(10)**, 105502/1. The simulations indicate that the predicted solidification temperature of the enclosed particle is lower than its bulk counterpart, but higher than that observed for clusters placed in vacuum. A comparison with a phenomenol. model indicates that, in the considered range of tube radii (RCNT) of 0.5 < RCNT < 1.6 nm, the solidification temperature depends

mainly on the length of the particle with a minor dependence on RCNT.

8.6 Growth Mechanisms and Oxidation Resistance of Gold-Coated Iron Nanoparticles

The Authors report the chemical synthesis of Fe-core/Gold-shell nanoparticles by a reverse micelle method and the investigation of their growth mechanisms and oxidation-resistant characteristics. The core-shell structure and the presence of the Fe and Au phases were confirmed by transmission electron microscopy, energy dispersive spectroscopy, x-ray diffraction, Mossbauer spectroscopy, and inductively coupled plasma techniques. S Cho, J Idrobo, J Olamit, K Liu, N Browning, S Kauzlarich, from the Department of Chemistry, Department of Physics and Department of Chemical Engineering and Materials Science, University of California, USA, *Chemistry of Materials* 2005, **17(12)**, 3181. Addnl., at.-resolution Z-contrast imaging and electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) were used to study details of the growth processes. The Gold shell grows by nucleating on the Fe-core surface before coalescing. The magnetic moments of such nanoparticles, in the loose powder form, decrease over time due to oxidation. The less than ideal oxidation resistance of the Gold shell may be caused by the rough Gold surfaces. However, in pressed pellet form, elec. transport measurements show that the particles are fairly stable, as the resistance of the pellet does not change appreciably over time.

8.7 Ultraviolet and Blue-Violet Photoluminescence of Gold Nanoparticles

J Zhu, Y Wang from the Institute of Modern Physics, School of Science Xi'an Jiaotong University, Xi'an, 710049, Peop. Rep. China, *Guangpuxue Yu Guangpu Fenxi*, 2005, **25(2)**, 235.

Suspended gold nanoparticles (size range 20-30 nm) have been synthesized via electrochemical method. The emission spectra of gold colloidal nanoparticles were studied at room temperature. Fluorescence occurs at UV and blue-violet wavelengths. Two emission peaks were observed at 377 nm and 459 nm, resp., when the corresponding excitation wavelength was at 220 nm. The emission peak at 377 nm increases with increasing particle d. or excitation intensity, whereas the emission peak at 459 nm decreases with decreasing excitation intensity or increasing the particle d., and disappears below the threshold.

With increasing the slit width, the intensity difference between these two emission peaks decreases and the ratio approaches 1. All these observed results are in agreement with the theory of self-organized random micro-cavity. It is indicated that the fluorescence emissions in UV and blue-violet wavelength regions are induced by the multiple scattering in a disordered gold nanoparticles system. And these photoluminescence features suggest the possible future applications in the areas of optical data storage and full color display.

8.8 Formation and Characterization of Gold and Silver Nanoparticles on Silica Nanospheres

Novel optical effects are expected by appropriately arranging metal nanoparticles on the surface of spherical insulating materials. Optical resonances of this nanostructures from near IR to the visible range may be tuned by adjusting the oxide size, size of the metal particles and the filling factor. P Miclea, H Hofmeister from the Institute of Materials Science, Department of Electrical and Information Engineering, Univ. Wuppertal, Wuppertal, Germany, *Molecular Crystals and Liquid Crystals*, 2004, **417**, 135. For a better control of the optical properties of such composite materials the best choice as oxide material is the monodisperse oxide particles. H₂O-sol. metal precursor complexes hydrogentetrachloroaurate and Ag acetate were employed. The optical properties of these materials correspond to their overall structure of nanoparticulate composites having a very low filling factor of the metal phase.

9 Refining

9.1 'Green' Leaching: Recyclable and Selective Leaching of Gold-Bearing Ore in an Ionic Liquid

The recovery of gold and silver from ore in an ionic liquid is reported for the first time. The 1-butyl-3-methyl-imidazolium hydrogen sulfate ionic liquid (bmim+HSO₄⁻) was employed, with iron(III) sulfate oxidant and thiourea added. J Whitehead, G Lawrance, A McCluskey from the Discipline of Chemistry, School of Environmental and Life Sciences, The University of Newcastle, Callaghan, Australia, *Green Chemistry* 2004, **6(7)**, 313. Selective extraction of gold (>85%) and silver (>60%) from powd. ore (of dominantly chalcopyrite/pyrite/pyrrhotite/sphalerite mineralogy) was achieved at room temperature in 50 h, with other lower-value metals present in the ore (Cu, Zn, Pb, Fe) extd. to only low percentages.

Gold extraction was similar to that achieved in aq. H₂SO₄/thiourea/Fe₂(SO₄)₃, and silver extraction was significantly better. Moreover, the ionic liquid can be recycled following selective stripping of gold and silver on activated charcoal, with reuse in at least four successive treatments leading to neither ionic liquid degrdn. nor any loss in extraction efficiency.

9.2 Heap Biooxidation of Refractory Gold Ores: Current State of The Art

A review on heap bioleaching of low-grade refractory sulfidic ores for Gold recovery. Varying the conventional operating parameters with leach flow rate, particle size, and bed height has little effect on sulfide oxidation beyond the av. of 10-15%/mo. S Bouffard, D Dixon from the Placer Dome, Inc., Vancouver, BC, Canada, *Mineral Processing and Extractive Metallurgy Review* 2004, **25(3)**, 159. The industrial bioleaching may be improved by process control with a

balance between the coarse and fine ore particles.

9.3 A Two-Stage Bacterial Pretreatment Process for Double Refractory Gold Ores

Double refractory gold concs. were subjected a two-stage microbial process to destroy both sulfides and carbonaceous matter. In the first stage, the well-known sulfide biooxidation process, which utilizes chemolithotrophic bacteria was used to oxidize sulfides, and in the second stage carbonaceous matter is destroyed by using the bacterium *Streptomyces setonii*. After biooxidation of sulfides in the first stage, cyanidation resulted in 81.1% gold extraction R Amankwah W Yen, J Ramsay from the Mining Engineering Department, Queen's University, Kingston, Canada, *Minerals Engineering* 2004, Volume Date 2005, **18(1)**, 103. The action of *Streptomyces setonii* in the second stage led to a reduction in the content of carbonaceous matter, which reflected pos. in the preg-robbing and leaching behavior of the sample. Degrn. of carbonaceous matter was affected by pulp d., temperature and retention time. After degrn. of carbonaceous matter, gold extraction increased by 13.6% and resulted in an overall extraction of 94.7%. The results depict a novel two-stage microbial process to degrade both sulfides and carbonaceous matter and increase gold recovery from double refractory ores.

9.4 Gold Recovery from Arsenical Ores and Wastes

A gold recovery process is described which was invented and developed to solve the oldest and largest arsenic problem in North America: the 200,000 to 250,000 tons of arsenic trioxide fume stored in mined out underground areas of the Giant Yellowknife Gold Mine/Canada. The process involves the reaction of ammonia with arsenic trioxide to produce ammonium arsenite and washing the solids for gold recovery. Gold recovery was found to be in excess of 99%. W Drinkard from the Drinkard Research and Development Corp. and Drinkard Metalox, Inc., USA, *Arsenic Metallurgy, Proceedings of [a] Symposium held during the TMS Annual Meeting, San Francisco, CA, United States, Feb. 13-17, 2005*, 301. The arsenic values were chosen to be collected as copper arsenate, which found a ready market in the production and sales of copper-chrome-arsenic wood preservatives.

9.5 Recovering Gold from Copper Concentrate Via The Hydrocopper Process

HydroCopper technology comprises a chloride-leaching method for copper sulfide concentrates and copper production up to semi-products. As compared with the commonly used sulfate solutions., brine solutions offer aggressiveness and stability of the copper(I) ion and, consequently, a lower energy consumption in leaching. Copper(II) ions and oxygen are used as oxidants. Iron reports to the leaching residue as oxide and sulfur as elemental

sulfur. Gold is dissolved and recovered in the third stage of the counter-current leaching when the redox potential reaches higher levels.

9.6 Gold in the Electrorefining of Copper and the Decopperizing of Copper Anode Slimes

Most byproduct gold comes from the processing of copper refinery anode slimes generated during the electrorefining of copper anodes. In the copper anodes, the gold occurs in copper solid solution During electrorefining, the copper dissolves, and the associated gold is released. Some of the gold reports as small gold particles in the anode slimes. The gold shows a strong affinity for the selenide phase, and some of the metallic gold nucleates on the selenide particles. Some gold also appears to dissolve in the sulfate electrolyte, possibly because of chloride and thiourea.

The dissolved gold subsequently precipitates as a minor constituent of a complex oxidized phase and reacts to form a solid solution in the selenide phase and discrete Ag-Au-Cu selenide phase. Removing of Cu from the anode slimes concs. the gold as metallic gold and Ag_3AuSe_2 phase. The metallic gold shows a strong affinity for selenium, and the Ag-Au selenide phase appears to form during Cu removal and become prevalent under high-temperature and pressure-leaching conditions. Also, the silver selenide phase becomes enriched in gold.

9.7 Solvent extraction of Gold from Ammonium Thiosulfate solution by Trioctylmethylammonium Chloride (2nd report). Extraction effects and Conditions of Ammonium Thiosulfate Solution

Leaching process by ammonium thiosulfate and solvent extraction by trioctylmethylammonium chloride (TOMAC, $(C_8H_{17})_3CH_3NCl$) to recover gold from ores and waste was developed in the authors lab. K Liu, A Shibayama, T Fujita from the Dep. Geosystem Eng., The Univ. Tokyo, Japan, *Shigen to Sozai* 2005, **121(2,3)**, 65. In this report, the effects of gold, pH ammonia, thiosulfate and cupric (Cu^{2+}) ion concentration of ammonium thiosulfate solution, org. and water phase ratio were investigated to obtain a high recovery of gold with TOMAC.

Under the const. condition of TOMAC (0.18 mol/L, n-octane diluent +10 vol% 1-hexanol (in org. phase)) as discussed in the 1st report which is related with this work, it was found that extraction efficiency increased with the thiosulfate ion to form a $(TOMAC)_3-Au(S_2O_3)_{23}$ -ion at the condition of 0.01 to 0.03 mol/L Cu^{2+} ion and 1.0 to 3.0 mol/L NH_3/NH_4^+ . From the experimental results, it is indicated that this process can recover gold effectively and directly from ammonium thiosulfate solution by TOMAC. In addition, the advantage of this process is that the extraction can be conducted without pH and other adjustment.

10 General

10.1 Commercial Aspects of Gold Applications: From Materials Science to Chemical Science

A review. Current industrial uses have provided a steady annual demand for gold of around 350-400 tonnes in recent years, the bulk of which is centered on electronics applications, with dental uses constituting the second largest application.

C W Corti, R J Holliday from the World Gold Council, London, *Gold Bulletin (London, United Kingdom)* 2004, **37(1-2)**, 20. Increased industrial demand for gold is only likely to come through the emergence of new applications (1) pollution and emission control technologies, including fuel cells (2) advanced electronics, elec. systems and devices (3) chem. processing of a range of bulk and esp. chems. using gold based catalysts (4) advanced coatings exploiting the novel properties of gold, particularly in nanoparticulate form (5) biomedical uses including medical treatments, drugs, implants, sensors and devices.

10.2 Preparation of Gold and Silver Nanoparticles and Their Use as Colorants

Review on preparation of Gold and Ag nanoparticles and their use as colorants. Issues relating to preparation of Gold and Ag nanoparticles with the object of using them in coatings is discussed. T Kobayashi from the Dep. R and D,

Nippon Paint Co., Ltd., Neyagawa, Osaka, Japan, *Journal of the Society of Inorganic Materials, Japan*, 2004, **11(313)**, 371. Main attention is paid to a process comprising the steps of using a protective colloid of a water-sol. comb-like polymer, dissolving it in an aq. solution of ion source contg. Au chloride and Ag nitrate, and then adding an amine under stirring to cause the reduction and formation of nanoparticles. A high-concentration stable paste of nanoparticles of Gold and Ag can be produced by such a method. Light absorption based on surface plasmons of Gold and Ag nanoparticles and application of Gold nanoparticles as colorants for coating are discussed.



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