ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Microstructural Dependence of Magnetic Properties of Pt/Co Multilayer Thin Films

High resolution electron microscopy was used to characterise the layer quality and crystallographic characteristics of Pt/Co multilayers, sputtered with Ar, Kr or Xe gases. Films prepared by Ar-sputtering were energetically bombarded by reflected Ar neutrals and consequently had smooth, continuous Co and Pt layers, but only modest (111) f.c.c. texture. Vapour-deposited and Xe-sputtered films, which experienced much less energetic bombardment, had superior (111) texture and sharp column boundaries, but had rougher Co-Pt layer interfaces. It was concluded that the superior (111) f.c.c. texture was responsible for a large magnetic anisotropy energy.

Magnetic Properties and Corrosion Resistance of Nb and Pt Doped TbFeCo Magneto-Optical Recording Films

The magnetic properties and corrosion resistance of Nb and Pt doped TbFeCo magneto-optical recording films were studied. The addition of Pt increased Fe sub-lattice magnetisation while the addition of Nb and Pt to TbFeCo caused no change in magnetic properties. A Pt and Nb doped TbFeCo film had high resistance against all types of corrosion and the magnetic properties were similar to those of TbFeCo. The carrier to noise ratio of the disk used as a TbFeCo/PtNb magneto-optical recording film was the same as that of the disk produced and used as a TbFeCo/PtNb recording film.

Mechanisms of the Various Nitric Oxide Reduction Reactions on a Platinum-Rhodium (100) Alloy Single Crystal Surface

The reduction of NO with H₂ was studied over a Pt₀.₃₃Rh₇₇(100) alloy surface used as a model catalyst for the automotive three-way catalyst. The mechanisms of the different reactions leading to the products: NO₃, NH₃ and N₂O are emphasised. The results showed that NO could be formed by combination of 2 N atoms at 350–1300 K if sufficient adatoms were available. Below 600 K the main contribution to N₂ formation was via NO(ad) + N(ad) → N₂ + O(ad). The selectivities to NO₃, NH₃ and N₂O were determined by the relative concentrations of NO(ad), N(ad) and H(ad) which vary with the experimental conditions.

Magnetic Properties of Multiple-Structure Multilayered Co/Pd Films

Co/Pd multiple-structure multilayered films, consisting of periodic piles of Co/Pd multilayered film layers and Pd thin-film layers were studied in order to improve the magnetic characteristics. By adopting such multiple structures, a squareness ratio of unity, coercivity of 2.5 kOe, and residual magnetisation of 1.5 kG were obtained for a thick film of 2000 Å.

Properties of Thin Palladium-Films and Their Hydrogen-Permeability

Thin Pd films were used as protective layers on cleaned less noble metals to protect them against reoxidation, and to allow easy H₂ uptake. Optimal preparation conditions for protective but H permeable films were investigated. H uptake from the gas phase is mainly determined by adsorption layers on the film surface, and H permeability is connected with film/substrate interface structure. Low deposition rates and increased substrate temperatures give Pd films with the best properties.

A Study of the Magnetic Properties of Gd₄Pd₃ in Applied Magnetic Fields

The low temperature heat capacity and magnetic susceptibility were measured on Gd₄Pd₃ and Gd₄Pd₄ compositions. The Gd₄Pd₃ was found to be a two phase alloy consisting of Gd₄Pd₃ and Gd₄Pd₃-GdPd eutectic. The Gd₄Pd₃ compound was confirmed to be antiferromagnetic with a Néel temperature of 18 K. Another magnetic transition was observed at -6 K which has characteristics of ferromagnetic or ferrimagnetic ordering. Heat capacity measurements on Gd₄Pd₃ in applied magnetic fields showed a magnetic anomaly at -13 K in an applied field of -5 T.

Surface Oxidation of Fe-40Cr-Pd, Fe-24Cr-5Mo-Pd, Pd Implanted Fe-40Cr and Ion Beam Mixed Pd-FeCr Alloys

A review is given of the surface oxidation of the above alloys. Pd segregates at the oxide/alloy interface of the Pd-containing Fe-Cr alloys oxidised in air at 400–500°C. Very thin oxide film can be formed on the Fe-40Cr alloys at 500°C by implanting Pd ions at doses of 10¹⁶ ions/cm². The oxide scale formed on the Fe-40Cr-Pd alloy at 900°C consisted mainly of Cr₂O₃.

(45 Refs.)
Oxidation Characteristics of Some Fe-40Cr-Pd and Fe-40Cr-Ru Alloys in Air at 900°C


Alloys Fe-40Cr-1Pd, Fe-40Cr-3Pd, Fe-40Cr-1Ru and Fe-40Cr-3Ru were oxidised in air at 900°C; their isothermal oxidation behaviours were investigated thermogravimetrically and the scale morphologies studied. Additions of 0.92 and 3.2 wt.%Pd to the Fe-40Cr alloy substantially decreased the oxidation rate. However, adding 0.90 wt.% Ru to Fe-40Cr had little effect on the oxidation rate, while adding 3 wt.% Ru resulted in a slight decrease in the oxidation rate. The improved oxidation resistance of the Pd-containing Fe-40Cr alloys is attributed to Pd, which segregates to the oxide-alloy interface during elevated temperature oxidation, and facilitates Cr diffusion.

Growth of Intermetallic Layers in the Iridium-Molybdenum System


The growth of intermetallic layers between Mo and Ir in Mo and Ir-0.3 wt.%W-0.006 wt.%Th-0.005 wt.%Al alloy was examined at 1473-1748 K in Ar and vacuum. Two intermetallic layers: IrMo and Ir,Mo, of approximate equal thickness were formed, and an equation for the total layer thickness formed during a 4 h exposure was found. The vapour phase transport of Mo as MoO3 in Ar and vacuum. Two intermetallic layers: IrMo and Ir,Mo, of approximate equal thickness were formed, and an equation for the total layer thickness formed during a 4 h exposure was found. The vapour phase transport of Mo as MoO3 may account for the growth of these intermetallic layers. The layers have resistance to attack by acids similar to that of Ir.

CHEMICAL COMPOUNDS

A Rapid and Convenient Synthesis of Tetrakis(Triphenylphosphine)Palladium(0) and -Platinum(0) Complexes by Phase-Transfer Catalysis


A general, facile and convenient method is presented for the preparation of tetrakis(triphenylphosphine)Pd(0) and -Pt(0) complexes using phase-transfer catalysis. The complexes can be produced in good yields from the corresponding dichlorobis(triphenylphosphine)Pd(II) and Pt(II) complexes.

New Molecular Superconductor, \( \beta-[\text{CH}_3]_4\text{N}][\text{Pd(dmit)}_2]_2 \)


High pressure resistivity studies on the title Pd complex have shown it to be a new molecular superconductor. The superconducting transition was observed above 6 kbar. The mid-point transition temperature is 6.2 K at 6.5 kbar. The structure is almost isomorphous to the high-pressure superconductor \([\text{CH}_3]_4\text{N}][\text{Ni(dmit)}_2]_2\).

The First Example of a Cycloocta-1,3-diene Ligand Bound to Rhodium; Crystal Structures of Rh(\( \eta^1\)-C,Ph,X)\( _2\)L (L = 1,3- or 1,5-C,Ph,X)


[Rh(\( \eta^1\)-C,Ph,X)Br]\_2, reacted with either cycloocta-1,3-or -1,5-diene under reducing conditions to yield mainly Rh(\( \eta^1\)-C,Ph,X)(1,3,C,H)_2 (1) together with \( \leq 15\%\) of Rh(\( \eta^1\)-C,Ph,X)(1,5,6,C,H)_2 (2). The crystal structure studies of both (1) and (2) showed that unsaturated bonds of both cyclooctadiene ligands are extremely short with C=C 1.343(36) and 1.322(19)Å, respectively, in comparison to 1.341Å in free cycloocta-1,5-diene.

Hydrogen-Stabilized Mg,RhH\(_{1,1}\) w ith Filled Ti, Ni-Type Structure


The synthesis and structural characterisation of Mg,RhH\(_{1,1}\), which is the first known compound in the Mg-Rh-H system are reported. The H stabilised binary compound has a filled Ti, Ni-type structure. Retrieval of H by desorption destabilizes the structure and leads to a so far unknown binary metal compound of composition Mg,Rh which crystallises with the Ti,Pd-type structure, a branch of the MoSi\(_2\)-type structure.

Osmium-(V), -(IV) and -(III) Complexes with Tetratetradentate Dianionic Chelating Ligands


Os(III) and Os(IV) complexes of the ligands salen [H\(_2\)salen = ethylenediamine(salicylidineimine)], bpc [H,bpb = 1,2-bis(pyridine-2-carboxamido)benzene] and bpc [H,bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene] were synthesised by reducing the corresponding trans-dioxoosmium(VI) complexes with PPh\(_3\). The structure of [Os\(_5\)V(salen)](O\(_2\)P\(_2\))\(_5\) was determined. Electrochemical studies of trans-dioxoosmium(VI) complexes in acetonitrile showed a reversible oxidation wave assignable to the oxidation of Os\(_5\)V to Os\(_5\).

An Improved Synthesis and Some Reactions of a Hydridobridged Ruthenium-Manganese Complex


An improved synthesis of the heterodimetallic complex [RuMn(\( \mu\)-H)(\( \mu\)-PPh\(_3\))(\( \eta^1\)-C,Ph,X)CO\(_2\)] (1) was described and the reactions of this complex with alkenes RCCR (R = Ph, H or CO\(_2\)Me) and with tertiary phosphines were studied. Complexes containing \( \mu\)-alkenyl ligands were obtained by the reaction of (1) with alkynes and the crystal structure of one of these was determined by X-ray analysis. Tertiary phosphines react with (1) to yield complexes which were monosubstituted at the Mn atom.

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The Synthesis of the First Decametal Nitrido Cluster: X-Ray Structure Analysis and \(^{15}\)N NMR Studies of \([\text{Pb}_2\text{P}]_2\text{N}[\text{Ru}_6\text{N}(\text{CO})_{16}]_2\) 

The first decametal monoanionic nitrido species \([\text{Ru}_6\text{N}(\text{CO})_{16}]^{-}\) (1) has been isolated cleanly from redox condensation of the hexanuclear nitrido cluster \([\text{Ru}_6\text{N}(\text{CO})_{16}]_2\) with \([\text{Ru}_6(\text{CO})_{16}]_2\). The \([\text{Ru}_6\text{N}]\) unit remains intact, giving a nitrido cluster with a tetra-capped octahedral metal framework known previously only for carbido or hydrido species. The cluster (1) may be prepared in several ways.

**ELECTROCHEMISTRY**

Electrochemical Immobilization of Enzymes. 3. Immobilization of Glucose Oxidase in Thin Films of Electrochemically Polymerized Phenols


Electrochemically polymerised films of phenol and phenol derivatives can be used to immobilise enzyme glucose oxidase in a thin layer at a Pt electrode. The immobilised enzyme retains its activity towards glucose oxidation and \(\text{H}_2\text{O}_2\) generated by the enzyme catalysed reaction of glucose with \(\text{O}_2\) can be detected at 0.9 V vs SCE. The responses of the electrodes towards glucose are analysed. Phenol was the best for immobilising glucose oxidase.

The Volatmetric Electrooxidation of Glucose and Glucose Residues Formed on Electrodispersed Platinum Electrodes in Acid Electrolytes


Electrodispersed Pt electrodes in 0.5 M \(\text{H}_2\text{SO}_4\) solutions were used to study the voltammetric electro-oxidation of glucose and glucose residues. Electroadsorbed residues formed depending on the adsorption potential and the surface characteristics. Weakly bound adsorbates formed mainly at potentials >0.1 V (RHE), and these react with the \(\text{O}_2\) dissolved in the electrolyte, giving a strongly bound adsorbate, showing that this type of electrode could be used in fuel cells for medical purposes.

Electrocatalytic Properties of Platinum, Rhodium and Iridium during the Peroxidicarbonate-Anion Electroosynthesis


Studies of electrocatalytic properties of Pt, Rh and Ir made in concentrated K carbonate and during the formation of peroxidicarbonate-anion showed a number of electrocatalytic active centres on Pt, Rh and Ir surfaces, formed as the result of anion adsorption on anodically formed oxide layers.

A Voltammetric Study of Dihydrogen Sorption Phenomena at Palladium-Platinum Alloys


A series of Pd-Pt alloy electrodes were prepared via the reduction of M(allyl)\(_2\) (M = Pd, Pt) with \(\text{H}_2\). Using dilute perchloric acid the electrochemical behaviour of the electrodes was examined in the \(\text{H}_2\) evolution reaction. The dependence of different sorption phenomena on alloy composition was examined.

Palladium and Its Alloys as Membrane Catalysts for Liquid-Phase Hydrogenation of Dehydroinalool


Studies of catalytic properties of Pd and its binary and tertiary alloys with Ru, Ag, Y, Sn, In, Sb, Re, Co, Ni, Ge and La, as membrane catalysts were performed for liquid-phase hydrogenation of dehydroinalool to inalool. Pd membranes containing 5–7 wt.% Ru showed the highest selectivity and activity during the hydrogenation. An increase of Ru content from 0 to 10% decreased the number of electrons in the d-band from 9.55 to 9.32 electron/atom. However, this decrease in alloy H activation ability was compensated by an increase in alloy activity on the substrates.

X-Ray Photoelectron Spectroscopy and Electrochemical Surface Characterization of IrO\(_2\) + RuO\(_2\) Electrodes


Electrochemical and surface studies of IrO\(_2\) + RuO\(_2\) layers on Ti prepared by thermal decomposition at 400°C of the chlorides dissolved in acid aqueous solution were made by various spectroscopic methods. The surface analysis by XPS showed surface enrichment with Ir while the in-depth composition profile by AES showed homogeneous distribution of components below the surface. Voltammetric curves show features which can be used quantitatively to analyse the surface as sensitively as XPS. Redox transition potentials in voltammetric curves do not vary linearly with surface composition, thus pointing to some possible "synergistic" effects.

Oxygen Reduction on a Modified Ruthenium Electrode


A study of the effects of Tl and Pb adsorbates on the modification of a Ru electrode was performed during \(\text{O}_2\) reduction in alkaline solution. A partially oxidised Ru electrode is inactive for \(\text{O}_2\) reduction. The Ru surface modified with Tl and Pb adsorbates gave rise to a four electron-reduction of \(\text{O}_2\). Once activated, the Ru retained its activity even in the absence of Tl and Pb ions in solution phase.
A Ruthenium(III) Analogue of the Model Peroxidase System: Ru(II)-EDTA-Ascorbate-H2O2 in the Catalytic Epoxidation of Unsaturated Hydrocarbons

The epoxidation of cis-cyclooctene, styrene and trans-stilbene by the title Ru(III) system was studied at 30°C and 0.1 M KNO3 in a 1:2 (v/v) mixture of H2O and 1,4-dioxane in acidic medium. The rate of the epoxidation was first order with respect to the concentration of the substrates, catalyst, ascorbic acid and H2O2 and inverse first order with respect to the H+ ion concentration.

PHOTOCONVERSION

Kinetic Studies of Interfacial Photocurrents in Platinum Chloroplasts

Kinetic studies of photocurrents generated in a photobioelectrochemical cell constructed from platinum chloroplasts entrapped on a fibreglass filter were performed using a Pt gauze- and an Ag/Ag chloride electrodes. Upon illumination, an oriented photocurrent was observed. In the low-frequency, linear region, the normalised photocurrent response was constant. However, the yield of photocurrent per frequency interval decreased with an increase (>100 Hz) in the flashing rate.

Significant Effect of Carbonate Addition on Stoichiometric Photodecomposition of Liquid Water into Hydrogen and Oxygen from Platinum-Titanium(IV) Oxide Suspension

The effect of the addition of several electrolytes on the photocatalytic evolution of H2 and O2 from Pt/TiO2 suspended in H2O was studied using a closed gas-circulating system with an inner irradiation quartz reactor with 400 W high pressure Hg lamp. The addition of carbonate into a Pt-loaded TiO2 suspension lead to the highly efficient photocatalytic decomposition of liquid H2O into H2 and O2 stoichiometrically.

Photocatalytic Decompositions of Carboxylic Acid Derivatives by Semiconductors

Aqueous solutions of acetic acid, acetamide and acetonitrile produced CO2 and H2 at 300 K when irradiated in the presence of semiconductors, such as Pt/TiO2, TiO2, ZnS, and CdS. Similar results were obtained for benzoic acid, benzamide and benzonitrile. Pt/TiO2 was the best photocatalyst in generating H2. Nitrile is believed to be transformed into carboxylic acid through the intermediary of amide.

Light-Induced Oxygenation of Saturated and Alkyl Aromatic Hydrocarbons Catalysed with Platinum Metal Halogenides

On exposure in air to light, alkanes and alylalkanes were oxidised in CH3CN solution and in the presence of catalytic amounts of PtCl3, PtCl4, RhCl3, and RuCl3 to give alcohols and ketones. Accumulation of cyclohexane oxidation products occurred with induction period, being especially large for photocatalysts PtBr64−, but they were totally removed after hydroquinone addition. During the induction period, the photo-oxygenation reaction was catalysed by metal complexes in low oxidation order.

The Reactivity of 1,2-Diketones during the Photoinduced Reduction of Water in Microheterogeneous Systems

An efficient light-induced reduction of water with H2 evolution at a quantum yield of 1.0 was achieved, by using negatively charged 1,2-diketone radicals. Pt catalyst H2PtCl6 reduced with H2 and stabilised with polyvinyl alcohol gave the best H2 output, and when reduced with trisodium citrate a four-times smaller output is achieved. If the product quantum yield is based on H atoms rather than H2 molecules then a quantum yield of 1.0 is achieved.

Photoinduced Electron and Energy Transfer in Soluble Polymers

An −1:1 copolymer of styrene and chloromethyl styrene containing polypyrpyridyl complexes of RuII or OsII were used to examine the existence of intrastrand photochemical electron and energy transfer. These polymers are soluble and the experiments show that long range energy transfer can occur on individual polymeric strands. Energy transfer occurs at high efficiency with the anthyl chain acting as a “molecular light pipe” in conducting energy in a spatially controlled way along the polymeric backbone.

Luminescence from Excited Tris(2,2’-bipyridine)ruthenium(II) Incorporated into a Silk Fibroin Membrane

Studies of the luminescence from the excited state of Ru(bpy)32+ (bpy is 2,2’-bipyridine) incorporated into a silk fibroin membrane showed that the emission lifetime of the Ru complex was longer (1700 ns) than the value (598 ns) in aqueous solution. This is probably due to the presence of a rigid binding site for the complex, composed of tyrosine residues. Quenching of the emission from the Ru complex/silk membrane by O2 in the H2O phase was observed. The emission intensity and lifetime were dependent on the humidity of the membrane.
Mixed Oxide of Ruthenium and Titanium as a Protective Film Material for Silicon Anodes in Photoelectrochemical Cells


A film of mixed Ru and Ti oxides coated on a Si anode protected it against photocorrosion during the photoelectrolysis of KCI and HCl solutions. The height of the Schottky barrier at the n-Si/ORT contact was estimated to be up to 0.9 eV. However, the efficiency of a real electrode with a Schottky barrier is less than predicted. Interlayer formation can be prevented by implanting the Si surface with B and by using an electrode with a n-Si/p'-Si junction as substrate. The light to chemical energy conversion efficiency in the n-Si/P'-Si/ORT/30%HCl/Pt cell was 6%.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition and Electrochemical Behavior of Palladium Particles at Polyaniline and Polypyrorrole Films


The electrodeposition of Pd particles at insulating polyaniline (PA) and conducting polyprpyrrole films in aqueous solution was investigated. Pd was electrodeposited from 0.01 M PdCl₂, containing HCl and HClO₄ acids. H adsorption and desorption and H evolution took place on the Pd particles at PA in its reduced insulating state. H oxidation was observed concurrently with PA oxidation to its conducting state.

Laser-Induced Chemical Vapor Deposition of Rhodium


Rh stripes were laser CVD on glass substrates from volatile Rh precursors Rh(CO),thd and Rh(CO),hfa (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato; and hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato). Stripe width of 15 to hundreds of μm and heights of 5>μm were observed. Stripe resistivities were 2–60 times that of the bulk material and became optimal at intermediate laser powers.

APPARATUS AND TECHNIQUE

Thin-Film Gas Catalytic Microsensor


A catalytic calorimetric gas sensor prepared by thin-film techniques, using a glass substrate covered with a thin layer of Pt metal (2–10μm) is described. A free standing microfilament of Pt was designed for low power consumption and small size giving high sensitivity, low operating temperature of -800°C and low thermal response time of <50 ms.
Hydrogen Loading of \([\text{Li}_2\text{O})(\text{B}_2\text{O}_3)_{x_2}\) \([\text{WO}_3]_2\)-Glasses through Electrolyte/Glass- and Palladium/Glass-Interfaces


Photochromatic \([\text{Li}_2\text{O})(\text{B}_2\text{O}_3)_{x_2}\) \([\text{WO}_3]_2\)-glasses with a high "latent" colour centre density of \(6 \times 10^{16} \text{cm}^{-3}\) were prepared and characterised. The Pd/glass samples were mounted into the same cell with the Pd side to the 2N HCl electrolyte; Pd was loaded electrolytically with H, giving H:Pd>0.9. When this H-loaded Pd covers the glass, a fast lateral coloration occurs by chemical conversion of the Pd/glass interface, but only when the electrolyte is in point contact with the glass. A spectrally broad "white" absorption is observed, due to a chemical process apparently coupled with blue coloration.

A Novel Pd-SiN\(_2\)O, Hydrogen Sensor of High Stability and Sensitivity


A H\(_2\) sensor with high sensitivity of 100 mV/dec at 50°C and high stability of \(<3\) mV/day was prepared by using a single layer of SiN\(_2\)O as gate insulator in a Pd-MISFET device. The device was mounted on a probe designed for monitoring the H permeation of pipe-line and vessel materials operating in acid environments. The resistance of anti-corrosion coatings could be controlled by using this probe.

Sensitivity of Pd/SiO\(_2\)/Si Sensor to Humidity


A MOS capacitor with a Pd electrode is the main element in a device for measuring small concentrations (0.1–100 ppm) of H\(_2\) in He. In this concentration range even a small humidity sensitivity of this structure is important. Studies of the effect of H\(_2\)O vapour on sensor yield showed that the sensor selectivity to H\(_2\) with respect to H\(_2\)O is about 3 \(\times 10^3\). The processes on the Pd gate surface were analysed.

Formation of Bulk Pd-Ni-P Metallic Glass by Use of High Pressure


A new method for preparing Pd-Ni-P bulk metallic glass using Ni\(_2\)P\(_3\) sintered in vacuum, then mixed with Pd at a nominal composition of Pd\(_{0.8}\)Ni\(_{0.2}\)P\(_{3.5}\) is described. The cast alloy was obtained after arc melting the mixture several times. After crushing the alloy was subjected to high pressure thermal treatment, at 3.0 and 5.5 GPa and 1273 K for 120 minutes. Spherical samples with diameters of 1.0–1.5 mm were obtained. The critical cooling rate for Pd\(_{0.8}\)Ni\(_{0.2}\)P\(_3.5\) was 10 K/s. Pressure promoted glass formation mainly by suppressing nuclei growth. In this way amorphous material can be obtained in bulk, three dimensional, forms; other known processes can only produce films, foils and powders.

Minimizing Chloride Interferences Produced by Combination Acid Digestion Using Palladium and Hydrogen as a Matrix Modifier in Graphite Furnace Atomic Absorption Spectrometry


Using Pd/Mg(NO\(_3\))\(_2\) and 5% H\(_2\), matrix modifier was examined for reducing chloride interference in mixed-acid digestion systems, used to identify trace metals in water samples by graphite furnace atomic absorption spectrometry. The chloride, which solubilises certain metals, can interfere with other elements. However, when 5% H\(_2\) is added to Pd/Mg(NO\(_3\))\(_2\) chloride interference is reduced. For As, Sn, Pb, Cd and Tl only with Pd/Mg(NO\(_3\))\(_2\) as modifier and 10 \(\mu\)L of 2% HCl suppressions of 15–90% occur, but when 5% H\(_2\) is added these are reduced to <5% for Pb, Cd and Tl and for Sn when Pd/Mg(NO\(_3\))\(_2\) and H\(_2\) is the modifier the suppression is reduced to <5%. H\(_2\) maintains the Pd in its reduced form and minimises or eliminates HCl interference.

Iridium Oxide Thin-Film Stability in High-Temperature Corrosive Solutions


The pH response of sputtered IrO\(_x\) film (SIROF) electrodes was tested after exposure to solutions of pH 4, 7 and 10 in a pressurised bomb at 200°C (15 bar) and 245°C (40 bar). The SIROF had a linear response of \(-53–58\) mV/pH at room temperature under various conditions. Other advantages included their ruggedness, small size, high voltage/low impedance output, and the low cost of fabrication. The ion-assisted deposition helped to maintain film adherence and continuity on the Al\(_2\)O\(_3\) substrates during exposure to 200°C solutions. These thin films are being considered as pH sensing electrodes for use in arduous conditions similar to those that could occur underground in potential nuclear repositories.

Development of a Sensor for the Detection of Nitrite Using a Glassy Carbon Electrode Modified with the Electro catalyst [Os(bipy)\(_2\)(PVP)\(_2\)Cl]Cl

[Os(bipy)\(_2\)(PVP)\(_2\)Cl]Cl where bipy=2,2'-bipyridyl and PVP=poly(4-vinylpyridine) was used to modify glassy C electrodes for use in planar flow cells and conventional electrochemical cells for reductive electrochemical detection of nitrite. The electrocatalyst accelerates slow nitrite reduction via a two-step reduction process resulting in a 70-fold increase in response compared to an unmodified electrode. A linear response range: \(5\times10^{-5}–1\times10^{-2}\) M nitrite was obtained, with a detection limit of 0.23 ng/ml for the planar flow cell and 0.023 ng/ml for a conventional electrochemical cell. Following assessment of its performance with respect to interference, selectivity and stability, the sensor was used for the determination of nitrite in saliva.
Role of Electron-Donating/Withdrawing Character, pH, and Stoichiometry on the Chemiluminescent Reaction of Tris(2,2'-bipyridyl)ruthenium(III) with Amino Acids
A postcolumn chemiluminescent reaction detector for underivatised amino acids using the electrogenerated title Ru complex is described. The electron-withdrawing/donating character of the R group attached to the α-C of the amine influences the chemiluminescence efficiency of the reaction. Stoichiometric studies of four amines gave a Ru:amine mole ratio of 2:1, with relative intensities of the primary amino acids tested varying by a factor of 3. The system can be used for amine detection after protein digestion.

JOINING
Ceramic-to-Metal Joints Brazed with Palladium Alloys
Pd alloys: 60Pd–40Ni, 30Au–34Pd–36Ni, 50Au–25Pd–25Ni, 70Au–8Pd–22Ni, 93Au–5Pd–2Ni and 82Au–18Ni, all in wt. %, were tested for brazing Si₃N₄ ceramics to Ni for heat engine applications. Wetting tests of alloys on Ti, Zr and Hf-coated Si₃N₄ were studied under vacuum. All the braze alloys wet the Ti-coated Si₃N₄ well; joints brazed with high Pd alloys had shear strengths near zero. Joints brazed with low Pd alloys had good shear strengths of 75–105 MPa from 20–500°C.

HETEROGENEOUS CATALYSIS
Transition Metal and Enzyme Catalyzed Reactions Involving Ammonia and Amines
A comprehensive review is given of Pt group metals catalysts involving heterogeneous and homogeneous reactions. The reactions include catalysed condensation of ammonia or amines with alcohols, addition of N-H bonds to alkenes, enzyme-catalysed addition of ammonia to alkenes, ammoxidation and carbonylation. (278 Refs.)

Catalytic Oxidation of Chloroacetonitrile over a 1% Platinum Alumina Catalyst
The complete catalytic oxidation of chloroacetonitrile over a 1% Pt/Al₂O₃ catalyst was studied in a fixed bed reactor at 275–400°C, atmospheric pressure and concentrations of 250–10,000 ppm (v/v) in humid air. A kinetic rate expression was developed to describe the data.
Hydrogenation of Aromatic Compounds over Noble Metals Dispersed on Doped Titania Carriers


The influence of doping the TiO₂ carrier on the metal-support interactions of Pt, Pd, Rh and Ru for hydrogenation activity, chemisorption and S tolerance during slurry phase hydrogenation of benzene, naphthalene and biphenyl was investigated. Dopants of higher valence than the parent cation, such as W⁶⁺ or Ta⁶⁺, were diffused at high temperature into the carrier. The H adsorption of Rh, Ru and Pd was enhanced upon doping, and the enhancement was a function of dopant concentration.

Heterogeneously Catalysed Cyclisation Reactions of Ethyne over Single Crystal Palladium and Palladium Catalysts


The unusual cyclisation reactions of ethyne on Pd single crystal and supported Pd surfaces are described and discussed with reference to analogous transition metal cluster chemistry. The molecular pathways during the reactions are constructed in great detail. A Cl₂H₂ tilted metallocyclopentadiene was a crucial surface intermediate in the reaction to form either benzene or heterocycles. The single crystal data enable predicitions to be made about supported metal catalysts and about new areas of catalytic chemistry. (33 Refs.)

Catalytic Chemistry of Supported Palladium for Combustion of Methane


Studies of the catalytic activity of Pd/Al₂O₃ during methane oxidation at high temperatures of >500°C showed the presence of at least two distinct O/Pd species. At 750–800°C, the first decomposition of PdO₂ species dispersed on pure Pd metal occurred. The second decomposition was at 800–850°C and behaved like crystalline PdO. At >500°C, methane oxidation occurs readily when the catalyst contains PdO. The results showed that the high temperature activity of a supported Pd containing catalyst is due to the ability of Pd oxide to chemisorb O.

Sulfur Poisoning and Regeneration of Palladium-Based Catalysts. Part I.-Dehydrogenation of Cyclohexane on Pd/Al₂O₃ and Pd/SiO₂-Al₂O₃ Catalysts


The catalytic activities of Pd/Al₂O₃ (1) and Pd/SiO₂-Al₂O₃ (2) were examined for cyclohexane dehydrogenation and on adding thiophene or H₂S into the feed gas. Catalyst (1) was less active than Pd/Al₂O₃ (3) for cyclohexane aromatisation in the absence of any poisoning additive. The thio-tolerance is smaller for Pd than for Pt. Decontamination by S-free feed was less efficient for (1); but regeneration under pure H₂ was more effective than for (3).

Oxidation of Propylene Glycol and Lactic Acid to Pyruvic Acid in Aqueous Phase Catalyzed by Lead-Modified Palladium-on-Carbon and Related Systems


Oxidation of propylene glycol and related compounds to pyruvic acid was performed in the presence of Pd/C catalyst modified by Pb, Bi and/or Te, in aqueous phase, pH=8 and at 90°C. Pd/C was inactive in the oxidation of lactic acid but it bound Pb onto the metallic Pd by a strong interaction. The resultant Pb/Pd/C showed activity for the selective conversion of lactic acid to pyruvic acid with initial rate of the oxidation being a maximum at Pb:Pd=0.3.

Selectivity Behavior in Catalytic Oxidative Carbonylation of Alkylamines


Alkyl carbamates were produced in good yields by oxidative carbonylation of alkylamines using transition-metal heterogeneous and homogeneous catalysts, Pd, Pd/C, Rh/C, Ru/C, PdCl₂(PPh₃)₂, Bu₄N[Ru(CO)₃]₂, etc. and NaI promoter. Synthesis of methyl N-methylcarbamate by oxidative carbonylation of methanolamine is reported for the first time using the Pd-NaI catalyst system.

Evaluation of Palladium-Impregnated on the Performance of a Vycor Glass Catalytic Membrane Reactor


The effect of Pd impregnation sites on the performance of catalytically active, tubular porous Vycor glass membrane reactors was studied during dehydrogenation of cyclohexane to benzene on membranes prepared either by adsorption of Pd nitrate onto Vycor glass (PM1) or by reaction of Pd allyl chloride dimer with H₂O-treated Vycor glass (PM2). PM1 showed Pd deposited mainly at the inner and outer surface of the glass tube whereas PM2 had a more uniform deposition of Pd throughout the membrane wall. PM1 showed increases in conversion from an equilibrium value of 30% to over 75%.

Catalytic Properties of Palladium Deposited on SiO₂-MgO, in Hydrogenation of Carbon Monoxide


Studies of the effect of SiO₂ modification by Li, Mg, La, B, Al, Zr, Ti, V, Mo, Cr, Mn, Fe, Co or Ni, on catalytic activity and selectivity of Pd/SiO₂ catalysts were performed during CO hydrogenation in HC- and O-containing compounds. Pd/SiO₂ catalysts modified with oxides of Li, Mg, La, Co or V showed higher selectivity in methanol synthesis, and catalyst modified with oxides of Zr, Al, Mg, La or Ti additionally showed higher activity than unmodified Pd/SiO₂ catalyst.
Preparation of Highly Active Palladium Catalyst Supported on Silica by Ion Exchange Method
The preparation of a highly active Pd/SiO₂ catalyst by ion exchange using various aqueous NH₃ solutions was investigated. The catalytic activity of Pd/SiO₂ prepared using 28% NH₃ solution (catalyst 1) decreased rapidly with time during benzene hydrogenation; however, catalysts prepared using NH₃ solution (catalyst 2) of concentration <1.0% had high initial activity which decreased slightly during benzene hydrogenation over 2 h. In DTA measurements catalyst 1 had a peak at 300°C based on NH₃ combustion, but catalyst 2 did not. For catalyst 2 Pd oxide on SiO₂ was easily reduced at low temperature and the metallic Pd produced contained some lattice defects. Thus low NH₃ concentration produced a highly active, stable Pd/SiO₂ catalyst.

Catalytic Oxidation of Naphthalene on Palladium in Cooperation with Copper(I)/(II) Redox Couple
A Pd/SiO₂ catalyst working with a Cu⁺/Cu²⁺ redox couple was used to oxidise naphthalene in a water and acetic acid co-solvent. The products were 1-naphthol, 1,4-naphthoquinone and (!)-2-formylcinnamaldehyde with a total yield of >78%, in which naphthoquinone was 40%.

Palladium-Based Diffusion Membranes as Catalysts in Ethylene Hydrogenation
Pd-23 at.%Ag and Pd-7.8 at.% H₂ diffusion membranes were prepared, characterised, examined for H permeation at 100-450°C, and used as catalysts for C₂H₄ hydrogenation. The permeability of Pd-Y was substantially better than that of Pd-Ag, and increasing temperature and differential pressure across the membrane improved the permeation rate. C₂H₄ self-hydrogenated on both membrane surfaces giving C₁-C₄ hydrocarbons, at up to 60% conversions. C deposition was worse on the Pd-Y membrane, and both sides of the Pd-Y membrane were enriched with Y.

Preparation and Characterization of PdO-MoO₃/γ-Al₂O₃
Three different procedures were used to prepare 20 forms of the title catalyst, in order to achieve close proximity between the Pd and Mo oxides. The best methods for preparation were coadsorption of [Pd(NH₃)₄]²⁺ cations and MoO₄²⁻ anions on γ-Al₂O₃, and adsorption of Mo(O₂⁺) on PdO/γ-Al₂O₃; these gave a strong interaction between finely divided Pd and Mo oxides, even at metal loadings as low as 2%.

New Rhodium Complexes Anchored on Silica and Modified Y-Zeolite as Efficient Catalysts for Hydrogenation of Olefins
The Rh complexes [RhCl(COD)L], [RhCl(CO)₂L], [Rh(PPh₃)₃L] and their corresponding cationic complexes (L = 2-триэтилсилпропил) aminocarbonylpyrrrolidine were covalently bound to SiO₂ and ultrastable Y-zeolite containing supermicropores. The complexes anchored on the zeolite showed a higher activity for alkene hydrogenation than the free complexes in homogeneous medium, with SiO₂-anchored catalysts being the least active.

Catalysts for Ammonia Synthesis Based on Potassium Salts of Ruthenium and Osmium Carbonylhydrides Supported on Active Carbon and Metallic Potassium
Some studies of K₂[Ru(CO)₅]+K (1) and K₂[Os(CO)₅]+K (2) catalysts supported on active C showed that the activities of (1) and (2) catalysts depended on the deposition temperature of the carboxyls on the support.

Chemisorption and Oxidative Interaction of Trimethylamine on Ru/TiO₂
The adsorption of trimethylamine (TMA) at room temperature and its oxidative interaction on TiO₂ and Ru/TiO₂ up to 773K was studied by FTIR. TMA was molecularly chemisorbed on the co-ordinatively unsaturated Ti⁴⁺ Lewis centres of the support at room temperature and is only slowly oxidised. A first oxidation leading to dimethylformamide (DMF), water and formate species occurs at 473 K on both samples. At 573K DMF is destroyed in O₂, giving nitrosyl species adsorbed on the Ru phase on Ru/TiO₂ and nitrate, water and formate on TiO₂.

HOMOGENEOUS CATALYSIS

Hydroformylation of 1-Hexene with Pt(P(C₆H₅)₂CH₂SO₃Na)₂Cl₂ and Its Tin Chloride Analogue on a Controlled-Pore Glass
The title Pt compound was supported on a controlled-pore glass to yield an immobilised olefin hydroformylation catalyst which reacted with excess SnCl₂ to yield, in situ, Pt(TPPPTS)₂Cl(SnCl₄) (TPPTS=trisulphonated triphenylphosphine). Normal to branch ratios of 11.5 were obtained for the hydroformylation of 1-hexene at 100°C and 1000 psig.
Palladium-Catalyzed Acylation of Amines Effected by Aryliodides and Carbon Monoxide


Studies of carboxylation of ArI (where Ar=n-NO,C,H,; Ph, o-MeC,H,; 2-thienyl and 2-naphthyl; R=n-IC,H,, P h, n-MeOC,H, and PhMeCH) in the presence of 0.5 mol% Pd(OAc), catalyst, NaOH, and primary amines RNH, under 1 atm CO at 60°C showed a production of amides corresponding to ArCONHR acid in high yields. Carboxylation proceeded at a high rate.

Catalytic Palladium-Mediated Tetraene Carbocyclizations: The Cycloisomerizations of Acyclic Tetraenes to Cyclized Trienes


Studies of Pd-catalysed carbo-cyclisation reactions of tetraene substrate with Pd(OAc), and PPh, in the presence of triene in 95% yield and good selectivity with >95% isomeric purity. Cyclisation proceeds with high diastereoselectivity and the cyclised product contains functionality which could be useful for further synthetic transformations.

Palladium-Catalyzed Synthesis of Amides and Peptides


The hydrostannolysis of the N-allyloxycarbonyl group was performed in the presence of Pd(PPh), and an activated carbonyl compound, forming a coupling product. The reaction proceeded very rapidly and in high yields. Peptides were synthesised in a one-pot procedure with no evident racemisation. This mild method seems applicable to synthesising a wide range of amides and peptides.

Control of Chemoselectivity in Catalytic Carbeneoid Reactions. Dirhodium(II) Ligand Effects on Relative Reactivities


When the ligand in dirhodium(II) catalysts is changed from perfluorobutyrate (pfb) to acetamide or caprolactam the dominant path of various reactions can be changed; for instance, the carbeneoid reaction can be transformed from aromatic substitution to cyclopropanation, from C-H insertion to cyclopropanation, from aromatic cyclo-addition to C-H insertion, and from aromatic substitution to carbonyl ylide formation. The choice of ligand markedly affects the product distribution from substrates in which intramolecular cyclopropanation and aromatic substitution are competitive. The chemoselectivity over a wide range of carbene transformation depends simply on changing the dirhodium(II) ligands from pfb to carboxamidine.

Mechanisms of the Formation of Isomeric Aldehydes upon Hydroformylation of n-Butenes in the Presence of Rhodium Catalysts


Kinetic and spectroscopic studies of hydroformylation and isomerisation of n-butene-2 in the presence of Rh,(CO), catalysts showed that pentanal formation occurred by two different routes: through isomerisation of n-butene-2 and n-butene-1 with their subsequent hydroformylation, and by isomerisation of alkyl- or acyl-catalytic complexes without elimination of n-butene-1.

The First Example of Carboxylation of Triarylbumethines: Remarkable Rhodium(I) Catalysis


Catalytic amounts of either [RhCl(CO),], or RhCl,(H),O were used for the reaction of triarylbumethines, Ar,Bi; Ar=C,H,, 4-MeC,H,, 4-MeOC,H,, 4-ClC,H,, with CO at atmospheric pressure, in acetonitrile, tetrahydrofuran or MeOH at 25°C. This produced the corresponding diaryl ketones in good yields, and also methyl benzoates in MeOH.

A New Type of Highly Active Polymer-Bound Rhodium Hydroformylation Catalyst


A new way of attaching phosphite to a (co)polymer chain is described, for preparing a Rh phosphate hydroformylation catalyst. This Rh polymer bound catalyst has activity identical to that of the low molecular weight analogue. The Rh catalysts show high activity for the hydroformylation of the otherwise unreactive cyclooctene. Only one phosphite is co-ordinated to the Rh complex in its active form.

Asymmetric Hydrogenation of Unsaturated Carboxyl Compounds Catalyzed by BINAP-Ru(II) Complexes. Enantioselective Synthesis of γ-Butyrolactones and Cyclopentanones


Asymmetric hydrogenation of 2- and 4-alkyldene-γ-butyrolactones and 2-alkyldieneecyclopentanones catalysed by BINAP-Ru(II) complexes affords the corresponding γ-butyrolactones and cyclopentanones in 94–98% ee. The hydrogenations of (E)- and (Z)-2-propyldene-γ-butyrolactone also catalysed by BINAP-Ru(II) gave products with the same absolute configuration and in almost equal enantiomericities, which shows that olefin geometry does not affect the stereochemistry and enantioselectivity.
Complexes of Ruthenium(II) and (III) Derived from O,N-Donor Ligands, and Their Efficiency as Catalytic Oxidants for Alcohols

New Ru complexes, [Ru"Cl,(PPh),L] (where L=benzoic hydrazide, bhz; substituted derivatives, R-bhz; R=p-Cl, p-CH3, o-NH, and phenylacetic hydrazide) and [Ru"X2(AsPh),C], where L'=mono-anions of 8-hydroxyquinoline, 8-hq; o-aminophenol; 2-amino-3-hydroxypyridine; X=Cl or Br) have been isolated. They were characterised spectroscopically and their redox behaviour was studied. The Ru(II) complexes were more effective catalysts than those of Ru(II) for primary alcohol oxidation to aldehydes and secondary alcohol oxidation to ketones in the presence of N-methylmorpholine-N-oxide as co-oxidant. Turnovers reached 400 with the catalyst [Ru"Cl,(PPh),] (8-hq).

FUEL CELLS

High Performance Catalyzed Membranes of Ultra-Low Pt Loadings for Polymer Electrolyte Fuel Cells

A new simplified process where thin film catalyst layers of ultra-low Pt loadings are cast directly from solutions of suspended Pt/C catalyst onto Nafion membranes at elevated temperatures (150–190°C) is described. Direct application seems to improve interfacial continuity between the ionomers in the membrane and in the catalyst layers, indicated by lower cell impedances. The casting solution and the membrane are in the Na+ form, to avoid acid-catalysed degradation of the ionomer at the higher casting temperatures used here; this gives more robust catalyst layers. The performance of fuel cells using these catalysed membranes is superior to others using low Pt loadings with PEM.

CORROSION PROTECTION

Corrosion Behaviour of Platinised Titanium during Reversal of Current in Sea Water

The rate of corrosion of platinised Ti electrode in sea water under various conditions of reverse current, and its dependence on current density and purity of reversal were studied in various ratios for periods of continuous anodic and cathodic polarisation. Current reversal caused an increase in the corrosion rate during the cathodic polarisation. The corrosion rate increased with an increase in current density and the duration of the cathodic polarisation.

Formation of Corrosion Resistant Surface Layers on Titanium by Sequential Implantation of Silicon and Palladium Ions

Studies of effect of implantation of 1017–1019/cm² of Pd ions on the corrosion resistance of Ti-Si layers was studied in 20% H2SO4 at 100°C. The presence of Pd in Ti substantially decreased the overvoltage of cathodic reaction of H yield, working as an effective cathode, and thus stabilised passivation of Ti substrate in the pores of the silicide layer. Pd implantation of Ti-Si layer increased its corrosion resistance by 2 orders.

CHEMICAL TECHNOLOGY

Copious Low Energy Emissions from Palladium Loaded with Hydrogen or Deuterium

The 100% reproducible emission of low energy radiation from Pd when loaded with D or H, by any loading technique, is reported. The radiations were observed from all the loaded samples. The D came from heavy water electrolysis and the H was commercially available. Autoradiography was the most used diagnostic tool, and all loaded samples fogged the X-ray films.

Deposition of Volatilized Ruthenium on Stainless Steels

Volatile Ru deposits have been prepared on stainless steel Types 304 and 321 substrates at temperatures of 150°C and above in conditions likely to occur during nuclear fuel processing: waste calcination and vitrification. Crystalline RuO2 was produced and no bonding with the steel surfaces occurred.

ELECTRICAL AND ELECTRONIC ENGINEERING

Rapid Isothermal Processing of Pt/Ti Contacts to p-Type III-V Binary and Related Ternary Materials

A detailed summary of the use of rapid isothermal processing to sinter Pt/Ti bilayer contacts to a variety of binary and ternary compound semiconductors is provided. Pt/Ti contacts to InAs and In0.53Ga0.47As were ohmic as-deposited, while the same metallisation scheme on GaAs, GaP, InP, In0.53Al0.47As and Ga0.7Al0.3As provided a rectifying contact as-deposited. Applying rapid thermal processing at 300°C for ternaries, and 450°C for GaAs, led to transition of these contacts to ohmic contacts.

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Infra-Red Surface Plasmons on Platinum Silicide


Surface plasmons supported on thin PtSi films in PtSi-Si Schottky diodes have been excited to more than 95% coupling efficiency with p-polarised IR light (3.392 μm) using a prism-air gap-sample configuration. The measurements were consistent with the calculated optical response. Stimulating surface plasmons optically offers a way to characterise silicide films and to enhance optical absorption in order to increase significantly the Schottky barrier photoresponse.

Shallow Ohmic Contacts to n-Type GaAs and AlGa1-xAs


Shallow ohmic contacts to n-GaAs and n-AlGaAs were formed by the sequential deposition of Pd/AuGe/Ag/Au and subsequent rapid thermal annealing at 450–550°C for 30 s. The metallisation on GaAs displayed good electrical properties with a contact resistivity of 2.0x10^-9 Ωcm² at a carrier concentration of 2x10¹⁷ cm⁻³. The contacts formed on Al₀.₅₅Ga₀.₄₅As had a contact resistivity of 2.1x10⁻⁸ Ωcm² at a carrier concentration of 7.5x10¹⁷ cm⁻³.

Van der Waals Bonding of GaAs on Pd Leads to a Permanent, Solid-Phase-Topotaxial, Metallurgical Bond


Weak Van der Waals forces usually provide an adequate bond between the native oxides of a III-V film and a new substrate. But when substrates were coated with Pd, a low temperature solid-phase-topotaxial reaction occurred producing oriented Pd,GaAs under the GaAs film. The resulting metallurgical bond is an ohmic contact, a thermal contact and a robust, permanent, adherent contact. Wafer bonding can be considered as a competitor to heteroepitaxial crystal growth for optoelectronic integration of dissimilar semiconductor material.

Low Stress Pd/Ge-Based Ohmic Contacts for GaAs Epitaxial Lift-Off


Ohmic contacts based on Pd/Ge show very low stress levels with comparable contact resistivity in comparison to traditional AuGe/Ni ohmic contacts on GaAs devices which suffer from high stress. Optimisation of the layers and processing parameters showed best results for Pd/Ge/Ti/Au combinations with short sintering times of 2 min at 340°C. MESFET structures were used as test devices for evaluation before and after epitaxial-lift off.

Backside Secondary Ion Mass Spectroscopy Study of a Ge/Pd Ohmic Contact to InP


High-resolution IMS depth profiles of Ge/Pd ohmic contacts on InP were obtained by sputter-etching from the back semiconductor side. At 200°C, a Pd-In-P alloy layer was formed at the contact interface but after subsequent processing at 325°C the alloy layer was partially dissolved as PdGe formed at the contact interface with regrowth of the liberated InP. The experimental studies suggest that regrowth is a key step in the formation of the ohmic contact.

Electron Beam Induced Metalization of Palladium Acetate


Pd(OOCCH₃)₂ thin films were stoichiometrically altered by exposure to electron beams of 1–30 kV, resulting in electrically conducting features with linewidths as narrow as 0.1 μm. The optimal dose and electron beam energy for 0.1 and 0.3 μm thick Pd films were 1 and 2.5x10⁻¹⁰ C/cm², and 4 and 5 kV, respectively. Resistivities as low as 100 μΩcm have been measured after post development heating to 180°C.

Selective Electroless Copper Metallization of Palladium Silicide on Silicon Substrates


A plating method for selective electroless Cu patterning of Si wafers was developed using Pd,Si which was easily formed from Pd layers on Si wafers. Pd,Si has good catalytic properties for electroless overplating. Excellent via-filling down to 0.5 μm dimensions and an aspect ratio of 6 was observed. The thin Cu deposited on the Pd,Si had a resistivity of ~0.2 μΩcm. Contactless photocarrier decay measurements indicate nearly no degradation of Si lifetimes by these processing steps.

Annealing Characteristics and Thermal Stability of Electron Beam Evaporated Ruthenium Schottky Contacts to n-GaAs


High quality Ru Schottky barrier diodes were fabricated on epitaxially grown n-GaAs by the electron beam evaporation of Ru. The effective barrier height and the flat band barrier height of the as-deposited Schottky contacts were 0.86 and 0.91 eV, and they reached their respective maximum values of 0.93 and 0.96 eV respectively, on annealing at 450°C in vacuum. Ru could be an excellent choice as Schottky contact material to GaAs because such contacts show good resistance to chemical attack, good diffusion barrier and thermal stability.