In a paper presented in 1942 at the 82nd ECS general meeting, Professor Peter J. W. Debye of Cornell University in New York presented an important extension of Smoluchowski's 1916 theory on reaction rates in ionic solutions. The earlier theory employed a purely diffusional treatment that Debye extended to include electrostatic effects arising from the presence of net charges. Debye, the 1936 Nobel Prize winner in Chemistry, derived the influence of intermolecular forces on reaction rates for dilute solutions (where Coulomb forces between the two reactants predominate) and for concentrated solutions (where other fundamental forces typical of strong electrolytes, including the screening effect, are important). Debye's research at this time was focused on macromolecular and colloid chemistry, and this new reaction rate theory was useful in understanding reactions such as the coagulation of colloid suspensions. It also clearly built on the mathematical and physical foundation of his numerous other publications on X-ray scattering, molecular dipole moments, molecular polarizability, electrolyte theory, and macromolecular light scattering.


Low Temperature Surface Cleaning of Silicon for MBE

Molecular beam epitaxy (MBE) can produce device quality Si films if the substrate is properly cleaned prior to epitaxial growth. High temperature (1200°C) thermal etching in ultra high vacuum (UHV) provides the required cleanliness but is often undesirable because it increases the densities of dislocations, stacking faults, and other defects. Further, it can result in unwanted thermal diffusion of impurities. In 1986, Akitoshi Ishizaka and Yasuhiro Shiraki of Hitachi in Japan described a low temperature cleaning method consisting of (1) wet chemical treatments to desurface and eliminate carbon contamination, (2) repeated wet chemical oxidation (boiling HNO2 and/or NH4OH:H2O2) and oxide removal (dilute HF) steps to further clean the surface, (3) formation of a thin, volatile oxide layer (via a brief dip in a boiling solution of aqueous HCl:H2O2), and (4) low temperature (< 800°C) desorption of the volatile oxide under UHV. Crystalline Si films grown on these substrates were shown to be of high quality by a combination of Auger electron spectroscopy, high-energy electron diffraction, and X-ray photoelectron spectroscopy.


The Shape of Electrochemical Polarization Curves

Polarization measurements are used to characterize the relationship between overpotential and current for electrode reactions. Early studies of electrode reaction mechanisms demonstrated that, in many cases, the current is exponentially related to the overpotential. In 1905, Tafel formulated the well-known equation that relates these quantities. However, in 1957, M. Stern and A. L. Geary of the Electro Metallurgical Company in New York observed that considerable uncertainty in the interpretation of polarization curves still existed. They published a theoretical study of polarization curve behavior for both noncorroding and corroding electrode systems. The authors concluded that deviations from Tafel behavior for a noncorroding electrode at low overpotentials are due primarily to the reverse reaction of the oxidation-reduction system, and at high overpotentials to concentration polarization and/or ohmic potential drop effects. For corroding electrodes, the forward and reverse reactions for both of the oxidation-reduction systems forming the corrosion couple were required to calculate polarization curves that reasonably explained experimental results published in the literature.


EMF Measurements on Galvanic Cells with Solid Electrolytes

As early as 1904, many researchers (including Fritz Haber) showed that electromotive force (emf) measurements on galvanic cells containing solid electrolytes would yield important thermodynamic information. In 1957, Carl Wagner (recipient of the Society's Olin Palladium Medal in 1951) and Kalevi Kuukkola of the Massachusetts Institute of Technology reported results of detailed emf measurements that allowed them to accurately determine the standard molar free energy of formation of CoO, NiO, Cu2O, Ag2O2, Ag2Se, PbS, and several phases of the Ag-Te system. In a typical experiment, a sandwich arrangement of three separate tablets (e.g., a mixture of a metal and its oxide, a ZrO2/CaO solid electrolyte, and a mixture of another metal and its oxide) was placed between two Pt disks. This cell was then placed in a furnace so that potentiometric measurements could be made at temperatures as high as 1150°C. The authors compared their emf and standard free energy values with literature results (both experimental and theoretical) and discussed possible causes for some of the observed discrepancies.


Surface-State Charge of Thermally Oxidized Silicon

In the early 1960s, the thermally oxidized silicon surface was the subject of intense investigation due to its extreme technological importance. In 1967, B. E. Deal (who was later honored as an ECS Fellow in 1991), M. Sklar, A. S. Grove, and E. H. Snow of Fairchild Semiconductor in California reported the results of an extensive experimental investigation of the effects of oxidation conditions, silicon orientation, annealing treatments, oxide thickness, and electric fields on the surface-state charge (Qss) of thermal oxide and on the spatial distribution of Qss within the oxide. Their experiments, primarily capacitance-voltage measurements on metal-oxide-semiconductor (MOS) structures, indicated that Qss is an intrinsic property of the silicon dioxide/silicon system and that it can be reproducibly controlled over the range 10^{10}-10^{12} cm^{-2}. The intrinsic nature of the surface-state charge was surmised from its relative immobility and by its high degree of reproducibility. The authors further concluded that Qss appeared to be due to an excess silicon species introduced into the oxide layer, near the silicon, during oxidation.


(continued on next page)
Acid Impedance Study of Li Diffusion in WO₃ Films

The electrochemical insertion of metal atoms into tungsten oxide is accompanied by a dramatic clear-to-blue color change caused by injection of electrons into the conduction band. This electrochromic phenomenon has been extensively studied and is the basis for several technological applications of these materials today. In 1980, C. Ho, I. D. Raisk, and R. A. Huggins of Stanford University in California reported the results of an electrochemical investigation into the thermodynamics and kinetics of Li-WO₃ electrochromism. They performed coulometric titration and ac impedance measurements on thin film WO₃ working electrodes immersed in a supporting electrolyte of LiAsF₆ in propylene carbonate. The counter and reference electrodes were pure Li metal. They observed that, at low ac frequencies, diffusion of neutral lithium limits the coloration rate of the oxide. At high frequencies, however, the kinetics of the electrochemical reduction of lithium ions was determined to be the rate-limiting step.


Structural Evaluation of Silicon Oxide Films

Silicon oxide films are extensively used in the fabrication of semiconductor devices. W. A. Pliskin (who was later honored as an ECS Fellow in 1991) and H. S. Lehman of IBM in New York produced an extensive study in 1965 that described a variety of physical and chemical analysis methods for characterization of oxide films. They demonstrated the utility of these methods by analyzing films formed by thermal oxidation, thermal evaporation, reactive sputtering, anodic oxidation, lead catalyzed oxidation, CO₂ oxidation, and thermal decomposition of tetraethoxysilane. Analysis was performed by a combination of infrared spectroscopy (in several frequency regions), selective etchants formulated from HF and HNO₃, optical interference microscopy, and electrical testing of oxide-passivated diodes. In addition to illustrating the power of this suite of characterization methods, the authors concluded that porous and strained oxides can be densified to be indistinguishable from thermal oxides, that steam is more effective than dry oxygen in densification procedures, and that surface hydroxyl groups can be removed by densification.


Thermodynamics of Electron/Hole Formation in Ge, Si, GaAs, and GaP

The forbidden energy gap of a semiconductor is the standard Gibbs energy for formation of electrons and holes. In 1975, C. D. Thurmond of Bell Laboratories in Murray Hill, New Jersey used data on energy gaps of Ge, Si, GaAs, and GaP to obtain the standard Gibbs energy, enthalpy, and entropy for electron/hole formation in these important semiconductor materials. Thurmond used previously published experimental data, of energy gaps of Ge, Si, GaAs, and GaP to obtain the standard thermodynamic functions for temperatures ranging from 0 K to the respective melting points of the semiconductors. Decreases in energy gaps with temperature are predominantly due to the relatively large entropies resulting from the interactions of electrons and holes with the lattice. The author also noted that the observed increases in enthalpies with temperature are indicative of positive heat capacity changes accompanying electron/hole formation.


Resistance for Flow of Current to a Disk

To avoid distortion of the potential field and the velocity distribution near a rotating disk electrode, the reference electrode is typically located some distance from the rotating disk. However, the ohmic drop between the reference and the working electrodes must be quantified. In a Technical Note published in 1966, John Newman of the Lawrence Radiation Laboratory and the University of California-Berkeley quantified the resistance between a disk imbedded in the surface of an insulator and a counter electrode located at a distance from the disk. They observed that the resistance is accompanied by a strong function of distance. Thus, to more accurately estimate the resistance between the reference and working electrodes (and therefore accurately quantify the ohmic potential drop), he concluded that it is better to locate the reference electrode some distance from the disk. Newman received the Society's Olin Palladium Medal in 1991 and was honored as an ECS Fellow in 1995.


Structural Features of Oxide Coatings on Aluminum

Anodization of aluminum in aqueous acid electrolytes produces oxide coatings that can be specifically tailored to suit the requirements of many different applications. Anodic oxides are used to improve corrosion, wear, and abrasion properties of structural aluminum alloys, and can also be used for decorative surface finishes. These oxides are also used as sensing elements in commercially-available capacitive moisture hygrometers and as ordered porous templates for fabrication of electronic, optoelectronic, photonic, microanalytical, and microelectromechanical devices. In 1953, F. Keller, M. S. Hunter, and D. L. Robinson of the Aluminum Company of America in Pennsylvania examined the structural features of oxides formed by anodization of aluminum in sulfuric, oxalic, chromic, and phosphoric acid electrolytes. Electron microscopy revealed that the coatings are comprised of close-packed cells of hexagonal oxide, with each cell containing a single pore. Pore morphology, pore size, and the thickness of both the cell wall and the barrier oxide at the bottom of the pore were all shown to be dependent on the anodization electrolyte and the forming voltage. Their pioneering work has had a significant impact on the aluminum anodization industry because it provided important information on processing-structure-property relationships for anodic oxide coatings.


Electropolishing Silicon in Aqueous Hydrofluoric Acid

Among the first investigations of the electrochemistry of silicon in hydrofluoric acid solutions was that by Dennis Turner of Bell Telephone Laboratories, Murray Hill, New Jersey in 1958. Earlier work by A. Uhlig, also at Bell Labs, had identified a divalent silicon dissolution reaction. Turner observed that this reaction occurred at current densities below that for the tetravalent silicon electropolishing reaction and produced a thick, solid layer in p-type silicon. The solid layer has since been identified as porous silicon, which remains today a material of great scientific and technological interest for applications in silicon-on-insulator circuit fabrication, chemical vapor sensors, microelectromechanical systems, and electroluminescent devices. Turner showed that the anode film contained fluoride ion and that hydrogen evolution occurred at the anode during the divalent reaction. He proposed that the divalent reaction produced an unstable silicon subfluoride that is oxidized to tetravalent silicon with concomitant production of hydrogen gas. Turner's proposed reaction is still generally accepted as the divalent electrochemical reaction that produces porous silicon. Turner was honored as an ECS Fellow in 1991 and received the Society's de Nora Award in 2000.

Lithium Intercalation into Carbon Electrodes

Carbonaceous electrodes have been widely used in rechargeable lithium batteries because of the well-established ability of carbon to intercalate large quantities of lithium to form Li$_x$C$_6$ ($0 < x < 1$). It is now generally agreed that the formation of a solid electrolyte interphase (SEI) at the surface of the carbon electrodes, as a result of the reaction of Li$_x$C$_6$ with nonaqueous solvents, plays an essential role in assuring the stability and the cyclability of such electrodes. The reaction between Li$_x$C$_6$ and nonaqueous solvents was observed more than a decade ago. In 1990, R. Fong, U. von Sacken, and J. R. Dahn at Moli Energy Limited in Canada reported the results of their study on this phenomenon using Li/graphite and Li/petroleum coke electrodes in a mixture of propylene carbonate and ethylene carbonate electrolyte. They found that the reactions were irreversible and only occurred on the first discharge of the cells. These irreversible reactions were associated with electrolyte decomposition and caused the formation of a passivating film or SEI on the surface of the carbon electrodes. The reactions proceeded until all the available surface of the carbon was coated with SEI. In subsequent cycles, these cells were found to exhibit excellent reversibility.


Ternary Phase Formation in Cathode Reactions of Lithium Batteries

Sulfides and oxides of transition metals have been exploited as cathode materials for ambient temperature batteries using lithium metal anodes. Very little was known concerning the cathode reaction mechanisms of these materials, or even of the reaction products, until 1976 when M. S. Whittingham of the Exxon Research and Engineering Company in New Jersey reported the results of his study on cell reactions between lithium and several transition metal oxides and sulfides. Whittingham found that ternary phases, rather than simpler lower lithium oxides or sulfides, as had been previously proposed, were formed during the cell reactions. The structure of the ternary product depended upon the crystal lattice of the initial reactant, and minimum structural change occurred during intercalation reactions. The reversibility of the discharge reaction was maximized when no chemical bonds were broken during discharge, as in the Li/TiS$_2$ system. When some chemical bonds were broken, as for V$_2$O$_5$ and TiS$_2$, partial or difficult reversibility was found. The Li/CuS cell exhibited only primary characteristics because all chemical bonds were broken during the discharge.


The All-Star List Continues...


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