INVESTIGATION OF ELECTRONIC STRUCTURE EFFECTS IN ELECTROMIGRATION
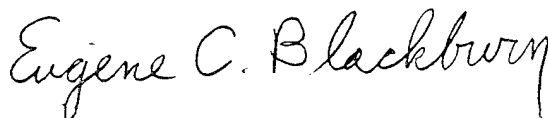
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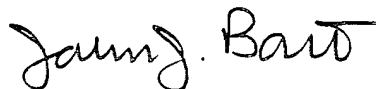
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13. ABSTRACT (Maximum 200 words)

The objective of this effort was to characterize the electronic structure of metal interconnects used in microelectronic devices for the purpose of better understanding electromigration in metals. Ideally, the approach would be to use available electron structure software to determine differences in total energy and density of states for the "ideal" metal and the "imperfect" metal. Changes in the electronic structure would then be associated with properties of the metal and compared with experimental systems reported in the literature. This technique would form a basis for evaluating proposed metal systems prior to actual fabrication.

Software available from the academic community was evaluated for suitability in the calculation of the electronic structure of microcircuit metallization. Three representative quantum chemistry software packages are described: (1) MOPAC, (2) GEOMOS, and (3) EHMACC. The limitations of the software are discussed and a suitable alternative for modeling electromigration presented.

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INVESTIGATION OF ELECTRONIC STRUCTURE EFFECTS IN ELECTROMIGRATION

ABSTRACT

The objective of this effort was to characterize the electronic structure of metal interconnects used in microelectronic devices for the purpose of better understanding electromigration in metals. Changes in the electronic structure of a metal are expected to occur at interfaces: (1) when a metal is bonded to another material during device fabrication, (2) because of impurities and defects in the crystal structure, and (3) due to physical and electrical stresses in the metal. One would expect the electronic structure to be sensitive to the type of chemical bond present at the interface as well as the internal structure of the metal. Ideally, the approach would be to use available electron structure software to determine differences in total energy and density of states for the "ideal" metal and the "imperfect" metal. Changes in the electronic structure would then be associated with properties of the metal and compared with experimental systems reported in the literature. This technique would form a basis for evaluating proposed metal systems prior to actual fabrication.

Software available from the academic community was evaluated for suitability in the calculation of the electronic structure of microcircuit metallization. Three representative quantum chemistry software packages are described: (1) MOPAC, (2) GEOMOS, and (3) EHMACC. The first, MOPAC is a semi-empirical molecular orbital package for investigating chemical structure and reactions. The second, GEOMOS, is a semi-empirical calculation package which provides alternative methods for

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treating the configuration interactions of the electrons. The third package, EHMACC uses an extended Hückel calculation algorithm. The limitations of the software are discussed and a suitable alternative for modeling electromigration presented.

Introduction

Electromigration is the major failure mechanism for current carrying interconnects and the primary hurdle to continued shrinking of silicon technology. A goal of electronic structure calculations in thin film conductors is to improve resistance to electromigration. Atomic movement can be slowed by reducing the grain boundary atomic flux, assuming lattice and surface diffusion are under control. The magnitude of atomic flux is determined by: (1) scattering processes, (2) grain boundary diffusivity, and (3) current density. The driving force is dictated by the scattering processes, which are intrinsic and not readily changed, and current density. The current density is a function of device requirements and the trend is towards higher current densities for smaller devices. Therefore of the three, the reduction in grain boundary diffusivity is the most practical method of increasing electromigration resistance [1]. For aluminum conductors, cumulative grain boundary diffusivity can be reduced by solute addition such as: Cu, Mg, Mn and Ti, or by elimination of grain boundaries using single crystal or bamboo structures. Single crystal metallization shows the greatest resistance to electromigration but there is no efficient process for growing single crystal aluminum films on oxidized silicon wafers. Bamboo structures have been used successfully, but these structures are more than an

order of magnitude less resistant to electromigration than a single crystal aluminum structure.

Since physical properties of metal films, such as Young's modulus and thermal conductivity, are determined largely by their morphology, changes in grain orientation influences the conductor physical properties as well as electromigration resistance. Thermal imaging using an atomic force microscope has shown that grain boundaries of current carrying Cu-Al films are hotter than the interior of the grains [2]. In addition, molecular dynamics simulation of aluminum surfaces, performed by Stoltz and Norskov, shows premelting of (110) surface layers at 200K below the bulk melting temperature [3]. This suggests the possibility of low activation energies for diffusion along grains having certain crystallographic planes parallel to the boundary. Impurities such as oxygen in the grain boundaries may have an even more dramatic effect on film transport properties. Work at Rome Laboratory suggests a correlation between oxygen concentration and void formation during electromigration [4].

In addition to the effects on physical properties, it is known that impurities also have a significant effect on electron scattering in metal films. On an atomic scale, impurities and other defects may cause significant variation in the periodic potential fields seen by the conduction electrons, and this distortion may extend a considerable distance from the center of the defect creating a large scattering surface for conduction electrons. The extent of this distortion in the periodic potential may be represented graphically by picturing the Bloch waves that describe the conduction electron density as the superposition of decaying sinusoids radiating out from each atom in the crystal. In a perfect crystal, the resulting interference pattern will have the periodicity of the lattice, but in

the presence of a defect (an interstitial atom or a vacancy, for example) there will be an extended region, centered on the defect, where this periodicity will be destroyed. This entire region must serve as a scattering obstacle. Grain boundaries would behave similarly but, in general, the degree of distortion would be much greater. This, of course, is an over-simplification of the distortion of the periodicity that occurs in a metal.

Electronic structure distortion is expected to occur where a metal is bonded to another material during device fabrication, at sites containing vacancies, impurity atoms, interstitials, dislocations, as well as at grain boundaries. The degree of intergranular electronic structure distortion will be influenced by grain orientation and the degree of atomic disorder resulting at the intergranular boundary. This intergranular electronic structure distortion will affect electron diffusivity and scattering at the grain boundary as well as the atomic diffusivity. It is expected that the electrical and physical properties of the film would be sensitive to these changes in electronic structure. Although the effects of physical structure changes on electromigration are well known, the significance of electronic structure changes to electromigration can only be estimated. Almost certainly the Al-Al_2O_3 interface perturbs the electron states of the aluminum metal near the interface, but how far into the metal does this perturbation extend? The width and thickness of the metal film is sure to be important in the overall contribution to I^2R (Joule heating) losses near this interface, and this loss of effective conducting cross section may become significant at small geometries. (The loss of effective conducting cross section could be as much as 5% for a 0.5 μm x 1.0 μm stripe and up to 21% for a 0.1 μm x 1.0 μm stripe assuming an oxide thickness of 10nm [4] on three sides.) The interface between the metal and the SiO_2 introduces another unknown

contribution to the degradation of the effective conducting cross-section at smaller geometries.

It would be instructive to investigate changes in the electronic structure of metal film systems, used in microelectronic devices, at defect/impurity sites. Ideally, existing electronic structure modeling software could be used to determine changes in total energy, density of states, band structure and material properties resulting from these changes in the electronic structure/states. Differences in properties of the simulated metal system from experimentally determined properties could then be compared with properties known to influence electromigration and other transport mechanisms. This technique, used as a part of design for reliability, could form a basis for evaluating proposed metal systems prior to actual fabrication.

Theory

Introduction of the Schroedinger Equation and Quantum Mechanics in the early part of this century gave chemists and physicists a powerful tool for studying problems that are mechanistically tied to the subatomic level [5]. Unfortunately exact solutions can be obtained only for a few systems. The few systems for which exact solutions have been found form the basis for approximating more complicated systems numerically.

Wavefunctions of the hydrogen atom can be used as a starting point in numerical calculations and modified using appropriate parameters to give the desired result. The wavefunctions of the hydrogen atom, however, are not as computationally efficient as some other functions which give equivalent results. The more popular functions include Slater Type Orbitals

(STO) and Gaussian Type Orbitals (GTO). The starting function is not critical, but does have a significant effect on computational time. Using the Self Consistent Field (SCF) calculation (developed by Hartree in 1928), the initial approximate wavefunctions are systematically modified to give the best approximation to the actual wavefunctions. One test of the "goodness" of the resulting approximation is the degree of agreement between the calculated and measured properties of the system being modeled [6].

There are a number of ways to determine wavefunctions all of which fall into one of two categories: ab-initio or semi-empirical. Ab-initio methods treat the core as the nucleus and use "all electron" calculations. Ab-initio techniques have the advantage of giving more accurate results for a wider range of material properties, but are much more computationally intensive and more restrictive in the size of the system (molecule) that can be investigated.

The semi-empirical methods treat the core as the nucleus plus the non-valence electrons. The interaction of the core electrons with valence electrons is then treated as the interaction of valence electrons with the "potential energy field" of the core [5]. The calculations are further simplified by replacing some of the interactions of the valence electrons by empirical data and neglecting many of the weaker electron interactions. Semi-empirical techniques allow studying systems containing much larger numbers of atoms than ab-initio techniques, but have a disadvantage in that semi-empirical techniques are tuned to certain physical properties and may be grossly inaccurate for computing other properties.

Software Selection

There are a number of quantum chemistry software packages available from the academic community. The University of Illinois has a software exchange program (QCPE) whereby it collects software from academia and redistributes it for a small fee to cover supplies and operating expenses. This software has the same capability as commercial, but is not as "user friendly." Most quantum mechanical software available is intended for molecular chemistry problems. Very few packages were found that specifically treated solids and none that modeled metals.

The intent of our task was to investigate rather large structures and the effects of impurities and/or defects, and to be able to use a workstation or a PC to do the calculations. Existing software was evaluated to determine its suitability to this problem. Ab-initio techniques could not be used because of the requirement to use small computers. The commercial software was not found to be computationally more efficient than academic software and offered no advantage other than a graphical interface for constructing the model and analyzing the results of the computation. As a result it was decided to use the academic software for our evaluation. Three software packages, MOPAC, GEOMOS and EHMACC, were evaluated for this task.

Software Descriptions

MOPAC is the core of a series of programs for the theoretical study of chemical phenomena. MOPAC is a semi-empirical molecular orbital package for investigating chemical structures and reactions, developed by

James J. P. Stewart, at the Frank J. Seiler Research Laboratory, U.S. Air Force Academy, Colorado. Molecular orbitals and heats of formation are determined and used in the calculation of vibrational spectra, thermodynamic quantities, isotopic substitution effects and force constants for molecules, radicals, ions, and polymers. Also calculable are transition-states. MOPAC comes with a detailed user's manual.

GEOMOS is a semi-empirical package developed by D. Rinaldi, P.E. Hoggan and A. Cartier, at Laboratoire de Chimie Théorique (U.A. C.N.R.S. no. 510), Université de Nancy I, Domaine Universitaire Victor-Grignard, B.P. 230, 54506 Vandouvre-les Nancy Cedex, France. The purpose of the GEOMOS program is the simultaneous determination of the relative position of the atoms in a molecule corresponding to a Slater AO basis and the desired assumptions about the electron interactions. It can be used for the elements with atomic numbers from 1 (hydrogen) to 54 (xenon). In addition, it allows the simulation of a solvent effect as well as the computation of a large number of physicochemical properties of the ground and excited states.

Included with GEOMOS is a program called GMHELP which queries the user for information needed by GEOMOS. GMHELP generates a data file containing all the information needed by GEOMOS, i.e., semi-empirical method used, geometry optimization, physical properties computed, bases of atomic orbitals, solvent effect, interaction with a planar surface, as well as initial coordinates of the atoms. For each question, GMHELP gives a set of possible answers and gives guidance in making the choice. The compatibility between the semi-empirical method used and the physical properties requested is tested, and the user can change requirements at any stage of the "conversation" to take the program's recommendations into

account. Data are entered unformatted, and GMHELP translates them into the appropriate GEOMOS format.

EHMCPP (Extended Hückel Molecular, Crystal and Property Package) is a set of programs for performing molecular-orbital calculations on molecules and band orbital calculations on solids. EHMACC was developed by M.-H. Whangbo, M. Evain, T. Hughbanks, M. Kertesz, S. Wijeyesekera, C. Wilker, C. Zheng, and R. Hoffmann. This package consists of three separate programs: EHMACC, EHPC AND EHPP described below.

EHMACC (Extended Hückel Molecular and Crystal Calculations) generates files used by the program EHPC to calculate the properties of a crystalline solid. EHPC (Extended Hückel Property Calculations) calculates the following properties:

1. the Fermi level

2. the density of states

3. the integrated density of states

4. the projected density of states

5. the crystal orbital overlap population

6. the total electronic energy

EHPP (Extended Hückel Property Plot) is a program for plotting the results of property calculations. The data can be plotted on the screen of a graphics terminal such as VT240 or VT330 or sent to a file in a format suitable for a plotter. This program is menu-driven, and runs interactively.

Results and Discussion of Evaluation

In general, all three of the above software packages were found to be unsuitable for the study of large atomic systems, in fact the problem we are investigating is beyond the capability of existing computers. Although installation of the software took some effort, once installed, running the calculations was almost trivial. The deficiencies of the software include small sample size, inaccuracy in the results of the calculations and the absence of time and temperature dependence in the model. In general, molecules on the order of 50 to 100 atoms are about the limit for this type of software on desktop computers, and stationary state calculations are all that can be done. It is true that the total energy of the system is one of the parameters provided by the software, and that many material properties depend on the total energy of the system. (The lattice constant, structure of point defects, grain boundaries and surfaces all depend on minimization of the total energy. Lattice vibration frequencies are determined from the curvature of the energy surface at its minimum. Activation energy for diffusion is the height of a barrier on the energy surface.) However, the cohesive energy of a metal represents only a small portion (less than 1%) of the total energy. This small percentage corresponds to a large error in physical properties such as melting point which are highly dependent on the cohesive energy [7].

The size of the structure being modeled is restricted by the long computation time required for large atomic systems. A small model consisting of 100 atoms can require several days of computation time on a 25MHz 68000 based workstation. Although computers available today are much faster than this, it will be sometime before collections of atoms

representative of real samples can be treated quantum mechanically on a workstation. Another limitation of the software investigated lies in the inaccuracy of the calculations. Both MOPAC and GEOMOS are based on empirical data that fit specific types of compounds, usually organic, and even then the results can be in error by 5 to 10%. EHMACC is intended for qualitative comparisons only. In any case, none of the software available can satisfactorily model metals.

Conclusions

For studying time dependent phenomena such as relaxation effects at grain boundaries, annealing characteristics at the atomic level or electron wind effects in electromigration a different approach must be used. During our investigation we found a technique that can be adapted to give quite accurate values for many physical properties of metals. This technique uses a more empirical approach which gives acceptable results for molecular crystals and ionic solids (closed shell). The particles are treated classically about their equilibrium positions in the solid and the cohesive energy determined from an interatomic force model based on the Van der Waals interaction, polarization of the atoms, in the case of an inert element such as argon; the Coulomb force between ions (in the presence of the electronic background) in the case of ionic solids such as sodium chloride; and the repulsive Coulomb and interatomic exclusion forces. These simple approximations are unacceptable for determining the cohesive energy and properties of covalently bonded materials and metals, but using effective medium theory it is possible to get good agreement with experimentally determined physical properties and also study time and temperature

dependent phenomena. This offers a viable solution to studying electromigration at the atomic level in the time domain on reasonably large atomic systems containing defects.

It was also determined necessary to begin our own simulation project. This project was begun under the AFOSR Summer Faculty program extended using an Expert Science and Engineering contract. The work continues under the AFOSR Basic Research for Device Reliability Task in the Reliability Physics Branch.

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