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Mass transport in single crystalline nano wires: Prediction of void formation based on the electron configuration of matrix and solute atoms

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Resumen

La resistencia hacia electromigración en pistas metálicas de la electrónica a nanoescala es comunmente aumentada por la impurificación con átomos de naturaleza específica. Nuestros estudios sugieren, que el estado intrínseco de carga eléctrica de vacancias en la red cristalina y de parejas entre vacancias y átomos disueltos es significativo en el proceso de la formación (o supresión) de huecos. En base a numerosos resultados experimentales, propios y publicados, de electromigración, hemos propuesto un modelo (una norma) semi empírico justificado teóricamente, que permite apreciar la probabilidad para la formación de huecos en la pista de una cierta combinación entre elemento matrix y átomo disuelto. Por razones de interés práctica orientamos atención particular a cobre, plata y aluminio como material de pista metálica, considerando una serie de elementos químicos para los átomos disueltos con alto potencial de generar o bien suprimir la creación de huecos.

Palabras clave: Electromigración, huecos, pistas metálicas, materiales cristalinos, metales puros, cobre, aluminio, plata, propiedades atómicas

Abstract

The resistance to electromigration of interconnect metals in nanoscale electronics is commonly increased by compounding impurity atoms of specific nature. These alloying additions are selected with the intention of maximizing the time to failure. Own studies suggest, that the intrinsic electronic charging state of vacancies and 'vacancy-solute atom' pairs in crystalline metals and dilute alloys is significant in the process of erosion void formation (or suppression). Supported by a number of own and published experimental electromigration data, a semi empirical rule is established here and theoretically justified, which allows a projection of the voiding probability of certain matrix element-solute atom combinations. Attention is paid to copper, aluminium, and silver as interconnect matrix metals, where chemical elements for solute atoms are singled out with a high potential of erosion void suppression.

Keywords: Electromigration, voids, interconnects, crystalline materials, pure metals, copper, aluminium, silver, atomic properties

Introduction

Mass transport in metallic interconnects, driven by electric currents, can lead to the nucleation and growth of voids. In dilute alloys, this process is intimately related to the coalescence of vacancy-impurity complexes. The formation of vacancy-impurity pairs in solids is abundant, and their bound state and joint migration has frequently been confirmed [1-4]. Numerous studies have shown, that voids are not static but move, they grow, even shrink or break and they change their shape in dependence on the direction of the electron flow. Whenever erosion voids are formed in metallic alloys under the action of the electron wind, an increased concentration of impurities on the inner void surface and around it is to be expected. Void migration toward the cathode side of the conductor, shape evolution and self healing of voids are most probably a consequence of the incorporation of vacancy-impurity pairs. Even transgranular slit voiding along certain crystallographic orientations, once initiated at a notch-site on a line edge could be caused by energetically preferred vacancy coalescence within certain crystal planes.

In contrast to the expectation by others, Prybyla and co-workers have suggested, that the inside of voids in Al(0.5wt.%Cu) near-bamboo grain interconnects after electromigration experiments with $2 \cdot 10^6$ A/cm² and elevated temperatures are free Al surfaces, and explain on the basis of Al diffusion along these void-surfaces the growth and migration of voids [5]. Given the alloying with Cu, X-ray spectromicroscopic or similar analysis data are required to exclude (for the support of their dynamic model of growth and void migration) the presence of Cu at the inner void surfaces. Similarly was a healing process after electromigration failure in submicron Al(0.5wt.%Cu) interconnects based on the existence of many small (~ 100 Å) metal islands, which remained in the voided region during void growth. These islands are supposed as made of Al, which during the thermally stimulated healing process coalesce [6]. Nevertheless is it not straightforward to suppose, that these metal islands are composed of Al, when the interconnects, exposed to electromigration, contained also copper. Here again, a micro chemical analysis would help to assure (or soften) the dominant role of Al in the described self reparation of the interconnect. If the interfacial mobility of copper is (presumed) equal to that of Al, then the healing effect of surface diffusion would be caused by either of them. In an effort to clarify the effect of segregated Cu on the overall grain-boundary diffusivity in Al(Cu) interconnects during electromigration, Liu et al. [7] studied a grain-boundary Frenkel pair model and corresponding diffusion mechanisms, adding to the established mobile defect mechanism via Schottky defects (vacancies) [8] a quite efficient transport process along grain boundaries via interstitials. Because of a smaller atomic radius (1.28 Å) compared to Al (1.43 Å), Cu segregates easily to interstitial sites. At Cu-stuffed Al grain boundaries, Cu is found to be more mobile than Al. On the other hand has been shown, that the binding energy of the Al-Cu dimer is stronger than those between Al-Al and Cu-Cu [7, 9]. In a recent paper of Srikar and Thompson [10] diffusion and electromigration of copper in single-crystal aluminium interconnects delivered data for activation energies of 0.8 eV, which are by far smaller than previously published values [11] for Cu diffusion through the Al lattice (1.4 eV). This allows to suppose, that the interface of Al with the surrounding SiO₂ is the dominant path for diffusion of Cu in single-crystal Al interconnects. Surface diffusion along the inner edge of voids can be concluded from measurements of Solak et al. [12], where enrichment of Cu in voids and particularly in grain boundaries on the downstream side of voids with respect to the electron flow in Al(4wt.%Cu) interconnects after electromigration was seen. Using sophisticated spectromicroscopic technique with a spatial

resolution of 100 nm and an energy resolution of 300 meV [13], the observation of microscopic changes associated with the electromigration process in interconnect lines is confidentially accessible. They also detect segregation of Cu to the interface between Al and the liner, confirming previous reports [14] on this subject. It is clear from these and other results, that the alloying Cu in Al(Cu) interconnects cannot be excluded from considerations, which elucidate dynamic or kinetic processes in and around erosion voids.

Model characterization

In a more general approach, we will consider a variety of chemically different alloying elements in aluminium, copper and silver. It will be shown, that the chemical nature of the solute atom in a metal matrix may determine in a decisive manner formation and suppression of voids. As a guiding parameter, we use in the present paper the electron configuration of matrix and solute atoms.

The formation and growth of electromigration voids in metallic alloys is a kinetic process. The corresponding kinetic equation can be formulated in analogy with the theory of nucleation [15]. We will characterize a void as a lattice complex, consisting of v vacancies, surrounded by s solute atoms. The number $N(v, s; t)$ obeys a master equation, where the transition rate from a $[v, s]$ -pair complex to a $[v+1, s]$ -pair complex due to coalescence of a vacancy with a void will be denoted by $\Pi(v+1, s; v, s)$. We suppose that the transition rate Π depends on the total flux J_v^{in} of vacancies into a sphere surrounding the $[v, s]$ -pair complex, and on the reaction rate Φ for the coalescence process

$$\Pi(v+1, s; v, s) = J_v^{in} \cdot \Phi \quad (1)$$

In order to form large $[v, s]$ -pair complexes, a permanent flux J_v^{in} is needed to bring a large amount of vacancies together. Such conditions are fulfilled in electromigration, but under otherwise identical conditions not in diffusion. The vacancy flux J_v^{in} is determined by the electron wind, the electric field force, electromigration-induced stress, and the deformation of the lattice due to vacancies and solute atoms.

We argue that the energy of the metal structure due to the lattice deformation will be minimized if the vacancies are trapped by solute atoms, and we describe this by an effective attraction potential between both. A consequence of such attraction is an increase in population of solute atoms around a $[v, s]$ -pair complex, as well as an attraction of vacancies by the $[v, s]$ -pair complex. Indeed results the attraction between vacancies and solute atoms due to the lattice deformation as an important argument for the fact, that (i) solute or impurity atoms are involved in the coalescence process of voids, and (ii) that the solute atom concentration is strongly enhanced around voids after electromigration [12,16-19].

Binding energies between nearest-neighbor vacancies and indium solute atoms embedded in an Al matrix have been measured by Epperson et al. [4], with a value of 0.29 eV. For triplets, consisting of two vacancies and one impurity atom, the value is 0.22 eV. The effective binding enthalpy between a vacancy and one or several identical solute atom neighbors in a larger range of concentrations in copper-germanium alloys has been determined by Hehenkamp and Sander [20] to be of 0.19 eV for the bound nearest-neighbor vacancy-single solute atom pair. The binding strength between a vacancy and solute atoms in an Al matrix was probed by Anthony [18] by means of impurity

concentration measurements in a vacancy precipitate after a temperature-step caused vacancy and solute atom flux. Depending on the chemical nature of the impurity atom, enrichment or depletion of the solute atom concentration around such vacancy precipitate pits (open voids at the surface) happens, indicating a different binding strength (drag) between vacancies and impurities embedded in the same matrix.

Rule definition

We have concluded, that, as a rule, the formation of electromigration voids is enhanced if the sum of the valence electrons of the matrix metal atom and the valence electrons of the alloying impurity atom is an even number. The formation of voids is suppressed in pure metals, and in alloys where the sum of the valence electrons of the matrix atom and the valence electrons of the alloying impurity atom is an odd number.

According to this rule, in a Cu matrix (valence $4s^1$) the presence of In (valence $5p^1$) or Ag (valence $5s^1$) does not prevent formation of voids in electromigration testing, but the presence of Sn (valence $5p^2$) does, as was really observed [17]. The same is known about Si (valence $3p^2$) in an Al (valence $3p^1$) matrix [21-23], or O (valence $2p^4$) in an Ag (valence $5s^1$) matrix [24]. Furthermore, the formation of voids in Au (valence $6s^1$) which was deposited on Ag is in accordance with this rule [25]. Careful experiments with Cu-doped Al proved strong void formation by electromigration, as was shown by Luby et al. [16] and others [19,22]. This is by no means in contradiction to the common praxis of alloying aluminium with copper in order to extend lifetimes in wide polygranular interconnects, where grain boundaries play a vital role in atomic transport. Mass transport via Frenkel-pair formation along grain boundaries was recently discussed [7], and gives a possible explanation, why Cu is so effective in terms of reducing grain-boundary diffusion in polycrystalline Al. The binding strength between a lattice-site vacancy and the solute atom plays an important role, and it obviously implies the geometrical structure in detail [26].

There are seemingly few cases, where accordance between prediction and experimental results of void formation in electromigration is violated, as displayed by the compiled data in Table 1. Moreover, the fact that no voids are observed as predicted might also be related to an insufficient testing time span.

In order to relate the reaction rate Φ from eq. (1) to the coalescence of a vacancy with a $[v, s]$ -pair complex, we stressed the importance of the electronic valence structure of matrix and solute atoms (as contained in Tab. 1). This rather involved problem of electronic structure, put up between matrix and embedded vacancies as well as solute atoms, has been treated by density functional approximations in the jellium model [27-29]. Indeed, the simple jellium model, where the delocalized valence electrons move in a homogeneous positive charge background (jellium) has long been used to study electronic ground-state properties of metals, and more recently also of small metal clusters [30-32]. The electron density $n(z)$ near the surface of the jellium experiences a steep, although not abrupt reduction toward the embedded vacancy. Several approaches for the calculation of $n(z)$ are known (see e.g. [28]). For a hole of radius r_h embedded in a jellium we choose the following set of spherical trial functions,

$$n(r) = n \{1 - 2\exp[-\beta(r-r_e)]\Theta(r-r_e)\} + \frac{1}{2} n (\cosh \gamma r_h)^{-1} \cdot \cosh \gamma r \cdot \Theta(r-r_e) \quad (2)$$

with $\theta(z)$ the Heavyside step function, and β the decay parameter of the electron density. For monovalent metals of electron density n , a void of v holes corresponds to a radius of $r_h = (3/4 v/\pi n)^{1/3}$. The two parameters in (2) are fixed by conditions of normalization and continuity of the first derivative. For further details see [28].

Matrix element, and valence electron state	Solute atom, and valence electron state	Valence electron sum	Void formation as predicted		Reference
			observed		
Cu 4s ¹	Ag 5s ¹	even	yes	yes	[33,34]
Cu 4s ¹	In 5p ¹	even	yes	yes	[33]
Cu 4s ¹	Nb 5s ¹	even	yes	yes	[35]
Cu 4s ¹	Sn 5p ²	odd	no	no	[33]
Cu 4s ¹	Ta 6s ²	odd	no	no	[36]
Cu 4s ¹	Pd 4d ¹⁰	odd	no	no	[37]
Cu 4s ¹	V 4s ²	odd	no	no	[38]
Al 3p ¹	Ag 5s ¹	even	yes	yes	[1]
Al 3p ¹	Au 6s ¹	even	yes	yes	[1]
Al 3p ¹	Cu 4s ¹	even	yes	yes	[10,12]
Al 3p ¹	H 1s ¹	even	yes	yes	[39]
Al 3p ¹	Ho 6s ²	odd	no	no	[40]
Al 3p ¹	Mg 3s ²	odd	no	no	[1]
Al 3p ¹	Na(?) 3s ¹	even	yes	yes	[41]
Al 3p ¹	Ni 4s ²	odd	no	no	[1]
Al 3p ¹	Si 3p ²	odd	no	no	[42]
Al 3p ¹	Ti 4s ²	odd	no	no	[42,43]
Ag 5s ¹	In 5p ¹	even	yes	no	[44]
Ag 5s ¹	O 2p ⁴	odd	no	no	[24]
Ag 5s ¹	Sb 5p ³	even	yes	no	[44]
Ag 5s ¹	Zn 4p ²	odd	no	no	[44]
Ag 5s ¹	Sn 5s ²	odd	no	no	[45]

Table 1: Comparison between predicted results for erosion-void formation, and observation of voids after electromigration testing, compiled from own and literature data. The valence electron state of each atom is included for rule testing: An *even* valence electron sum means 'probably void formation', an *odd* valence-electron sum means 'probably no void formation'. The two cases of silver, where void formation is predicted but not seen in the experiment, could well be caused by a too short testing time, and are not considered to contradict the model.

Immigration of electrons into the vacancy, and effectively charging it is a consequence, which turns out to be important for migration and coalescence of voids. A detailed calculation of the electronic structure of vacancies in aluminium delivered an effective negative charge of the vacancy of about 0.2e [27]. Due to polarization effects, a positive

charge density in the surrounding matrix is generated, which is commonly described by a screening of the fields due to the dielectric function $\varepsilon(q, \omega)$. With k_{TF}^{-1} the Thomas-Fermi screening length, the potential energy between two point charges within the electron gas-jellium system is given by [28,29]

$$U(r_{12}) = e_1 e_2 \exp(-r_{12} k_{TF}) / r_{12} \quad (3)$$

It is this Coulomb repulsion between vacancies or $[v, s]$ -pair complexes, which leads to the formation of a barrier and counteracts their coalescence. In pure metals with a perfect lattice structure the formation of voids is thus suppressed, in complete accord with the above cited experimental data. Nevertheless, at small distances, say of the order of a lattice spacing, the gain in energy by the reduction of surface energy may dominate, and once the barrier is surmounted, vacancies will coalesce.

The substitution of a matrix atom by a solute atom results in two effects. The lattice will be distorted, and we argued that this structural effect leads to an effective attraction between the solute atom and the vacancy. Furthermore, the electronic structure is changed because the valence of the host element is substituted by the valence of the solute, i.e. additional electrons are introduced by the solute atom which can move near the impurity site. The number of these additional electrons is equal to the difference between the solute- and matrix valence. Let us assume, that these additional electrons move on orbitals near the solute atoms. Paired electrons are relatively strongly bound to it, while unpaired electrons are not and may be treated as an additional contribution to the electron density near the impurity. Such increase of the electron density also yields an increase of the effective charge slipped into the vacancy. In a simple estimation the additional unpaired electrons may be assumed to be distributed homogeneously within the sphere of the z neighboring atoms so that the density as well as the effective charge of the vacancy are enhanced by a factor of $(z+1)/z$.

Conclusions

The electron configuration of matrix- and solute atoms affects in a characteristic manner the process of electromigration-provoked erosion void formation in metallic conductors. On the grounds of spin compensation (paired or unpaired valence electron state) a rule is established, that the formation of electromigration voids might be suppressed in dilute alloys, where the sum of the outermost (valence) electrons of the matrix atom and the alloying impurity atom is an odd number. As an unpaired electron of a solute atom (or an impurity) is partially trapped by a near-by vacancy, the effective charge e_v of the vacancy is enhanced. The most important aspect here is that those vacancy-solute atom pairs experience an enhanced Coulomb repulsion. The probability of coalescence is then diminished. This fact is demonstrated with numerous data compiled in Tab. 1. We have to remind of course, that the described void-suppression mechanism is bound to single crystalline- or at least bulk-electromigration through large grains. Grain-boundary transport follows different rules, as is best seen with wide Al(Cu)-alloy interconnects. On the other hand might future nanowire concepts point toward single-crystalline and ordered molecular configurations [46].

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