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Ab initio calculation of electromigration effects at polyvacancy clusters in aluminum

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The driving force on a migrating atom at polyvacancy clusters in aluminum is calculated using an *ab initio* multiple-scattering Green's function method. The open structure of polyvacancy clusters is considered as a model to simulate electromigration over a surface and as a start to simulate electromigration along a grain boundary. A random isotropic distribution of vacancies tends to decrease the driving force. In a configuration which resembles an atom on a surface the decreasing tendency is reinforced. In a configuration which resembles the situation at a grain boundary more specificly the vacancies are concentrated on the line along which an atom migrates. For such a configuration the force tends to increase.

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I. INTRODUCTION

The process of the drift of atoms due to an applied voltage, called electromigration, is studied both in materials science and in fundamental physics. The development of voids at the cathode side of an aluminum film and the growth of hillocks at the anode,[1] which is due to self-electromigration, shorten the lifetime of an integrated circuit. This process is commonly attributed to migration along grain boundaries. In the electronic industry a great deal of effort is made in slowing down this process.[2] In the present paper we report about a microscopic study of electromigration in polyvacancy clusters. For a certain cluster shape the results obtained can be considered as a first step in the direction of a microscopic description of electromigration along a grain boundary.

In the theory of electromigration one concentrates on the calculation of the driving force,[3–7] which is commonly written as a sum of two components, a direct force $\mathbf{F}_{\mathrm{direct}}$ and a wind force $\mathbf{F}_{\mathrm{wind}}$. The direct force is due to a net charge of the migrating atom, while the wind force is due to scattering of the current-carrying electrons off the atom. Both forces are proportional to the electric field and can be characterized by a valence,

$$\mathbf{F}=(Z_{\mathrm{direct}}+Z_{\mathrm{wind}})e\mathbf{E}=Z^{*}e\mathbf{E}. \tag{1}$$

The effective valence Z^{*} is the measurable quantity. The net charge is the result of incomplete screening by the electrons, which usually leads to a net positive charge and migration towards the cathode. However, in most cases electromigration towards the anode has been observed.[2] This has led to the conclusion that the direct force is dominated by the wind force. The wind force is proportional to the current density and therefore inversely proportional to the sample resistivity ρ, so that Z^{*} can be written as

$$Z^{*}=Z_{\mathrm{direct}}+\frac{K}{\rho}, \tag{2}$$

in which the temperature-independent proportionality constant K is determined by the scattering of the electrons by the migrating atom.

Up to now mainly metallic bulk calculations have been made.[3,5] Regarding electromigration at a grain boundary Sorbello has shown that a reduced electronic charge density along a grain boundary leads to a reduction of the wind force.[8] We will return to this contribution in the discussion of our results. Recently, Dannenberg and King calculated the wind force on a grain boundary as a whole, using a relation between the wind force and the contribution of a grain boundary to the electrical resistivity.[7,9] Although the subject of the latter study is related to the present one, migration of an atom along a grain boundary requires a more detailed treatment than the global process of migration of a grain boundary as a whole. In both studies the electronic structure of the metal around the grain boundary was modeled by a jellium. An account of the full metallic electronic structure at the electromigration defect is rather involved. That is certainly why complete microscopic calculations are mainly restricted to impurity migration in metallic bulk.[5,10] The present microscopic calculation of the wind force at a grain boundary can be considered as a first step, because a metallic bulk approach is still followed. Nevertheless, by removing an increasing number of atoms around the migrating atom more and more vacancies are introduced, and a more open structure is simulated. Such an open structure is one of the characteristics of a grain boundary. It has been shown already that the replacement of host atoms near the migrating atom by impurities affects the wind force.[11] This is the consequence of scattering of the applied current by the impurity, which changes locally its direction and the strength of current. Such multiple-scattering effects can be huge, sometimes even inverting the direction of the wind force.[6,12] The same effect is studied here for the addition of vacancies instead of impurity atoms. The formalism used accounts for the electronic structure at the electromigration defect as complete as possible at the moment.[5]

In Sec. II the ingredients of the formalism are mentioned, but it opens with a historical account showing more explicitly the complexity of the problem. In Secs. III and IV the results are given and discussed respectively. Section V gives conclusions.

II. THEORY

First we want to point at the complexity of the electromigration problem, which can be illustrated nicely by looking

at the quantum-mechanical expression for the wind force on an atom at a position $\mathbf{R}_p$,[13]

$$\mathbf{F}_{\text{wind}}(\mathbf{R}_p) = -\int \delta n(\mathbf{r}) \nabla_{\mathbf{R}_p} v_p(\mathbf{r}-\mathbf{R}_p) d^3r$$

$$= \sum_k \delta f(k) \langle \psi_k | -\nabla_{\mathbf{R}_p} v_p | \psi_k \rangle. \qquad (3)$$

This equation traces back to the pioneering work of Bosvieux and Friedel.[14] It contains the deviation from equilibrium $\delta n(\mathbf{r})$ of the electron density at $\mathbf{r}$, the potential of the migrating impurity v_p as felt by the electrons, and the electron wave function ψ_k at the migration defect. The label k combines the band index n and the crystal momentum $\mathbf{k}$ of the electron. One notices two different ingredients, one requiring the treatment of a local scattering problem and another one requiring solution of the electronic transport problem. Locally one has to evaluate the matrix element of the force operator $-\nabla_{\mathbf{R}_p} v_p$, to which end the electronic structure problem, being an equilibrium problem, has to be solved. The transport problem is usually handled by solving Boltzmann's equation and by which the occupation $f(k)$ of the electron states is obtained. This can be written as

$$\delta f(k) = f(k) - f_{\text{FD}}(k) = -e\tau \mathbf{E} \cdot \mathbf{v}_k \delta(\epsilon_{\text{Fermi}} - \epsilon_k), \qquad (4)$$

in which $f_{\text{FD}}(k)$ is the equilibrium Fermi-Dirac distribution function, $\delta f(k)$ is the deviation due to the presence of an electric field $\mathbf{E}$ being proportional to the transport relaxation time τ, and $\mathbf{v}_k$ is the velocity of the electron in the state k. Since $f_{\text{FD}}(k)$ obviously leads to a zero contribution to the electric current in the system, so to the "wind," only $\delta f(k)$ appears in Eq. (3). In the past 40 years progress has been made in dealing with the local problem, but the progress developed rather slowly. Besides the free-electron-model treatment by Bosvieux and Friedel,[14] for many years the model-pseudopotential treatment by Sorbello[3] was the only available one, being applicable to simple metals and weakly scattering impurities only. The first *ab initio* treatment is due to Gupta,[4] which was based on multiple-scattering theory. Regarding the evaluation of the wind force at an arbitrary position $\mathbf{R}_p$ of the migrating atom along its jump path, Gupta's treatment was still approximate, which was illustrated most clearly by the formulation of the full theory published somewhat later.[15] That is probably why Gupta restricted himself to just a few applications.[4,16] The solution of the problems involved has been presented only recently.[17,18]

In the Green's function approach at present available the electronic structure of the host metal and of the electromigration defect are accounted for as complete as possible. The potentials used are constructed *ab initio*, and the wind force can be calculated at an arbitrary position along the migration path. The bulk results appear to be reliable and compare well with experiment.[5] Recently this microscopic Green's function description has been generalized such that electromigration of atoms on surfaces can be studied.[19,20] No calculations have been made yet for atoms at a grain boundary, which is certainly due to the complexity of the defect. In the present work we model a grain boundary by omitting more and more atoms in the local atomic cluster, in which the electromigration takes place. Because this local cluster is embedded in an infinite lattice of unperturbed metallic host atoms, this model can be considered as a bulk simulation of the open structure of a grain boundary. The approach is applied to aluminum.

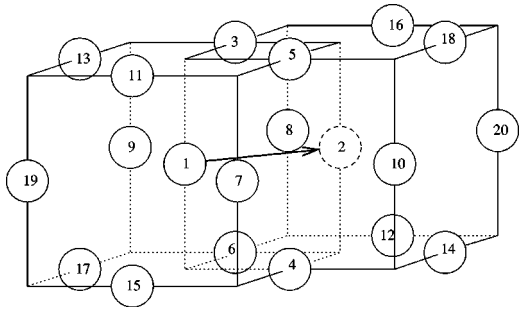

FIG. 1. The cluster of perturbed atoms in the FCC structure. The labels of the positions are used in the text. The wind force on the atom labeled by 1 is calculated at several positions along its jump path to the vacant position labeled by 2. By omitting an atom at another position a vacancy is added.

III. RESULTS

The atoms in the local perturbed host cluster, which is shown for the fcc structure in Fig. 1, can be chosen freely. This cluster of 20 atoms represents the first shell around both the initial and final positions of the jumping atom. Some of these positions are left unoccupied, giving the additional vacancies. All positions in the cluster, except the one of the jumping atom labeled by 1, are assumed to be exact lattice positions, so no relaxations are taken into account. On the other hand, the electronic structure is accounted for, so the much more important charge transfer effect, leading to different atomic potentials even if they represent host atoms, is taken into account fully.

The work done by the wind force (3) must be averaged over all possible jump directions, leading to a force which is proportional to the electric field $\mathbf{E}$ and to the scalar quantities Z_{wind} or $K = \rho Z_{\text{wind}}$ according to Eq. (1) and (2). The temperature-independent quantity K is used to characterize the wind force throughout this paper. Path-averaged values are obtained by calculating the force at ten positions along the jump path, which is assumed to be straight.

The bold line in Fig. 2 shows the variation of this quantity along the path for a jumping Al atom. It varies from $-25\ \mu\Omega$ cm in the initial position to $-63\ \mu\Omega$ cm halfway along the path. The latter position is called the saddle point position. The average over the path is $K = -39\ \mu\Omega$ cm. The other curves in the figure correspond to configurations with an additional vacancy at one of the positions 3–20 in the cluster displayed in Fig. 1. It is clear that the wind force depends on the position of the vacancy. When the vacancy occupies position 19, $K = -42\ \mu\Omega$ cm, whereas a vacancy at position 3 leads to $K = -21\ \mu\Omega$ cm. This difference of a factor of 2 is the result of the local currents arising from scattering of the incident host current by the vacancies. A vacancy at position 7 has a relatively large influence on the

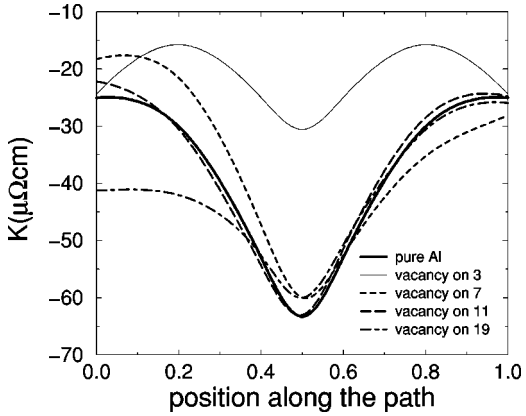

FIG. 2. Variation of K for a host Al atom with an additional vacancy at one of the positions in the perturbed cluster. The labels of the positions correspond to those in Fig. 1.

wind force at each position along the path. It leads to a smaller wind force at the first half of the jump, but in the second half it enhances the force. On the average a vacancy on this position only changes the wind valence to $K=-36\ \mu\Omega$ cm. Taking the average over all configurations with one extra vacancy and assuming equal probability for each of these 18 configurations, one finds $K=-34\ \mu\Omega$ cm. So the increased vacancy concentration at the grain boundary is expected to diminish the wind force.

The large value of the wind force for a vacancy at position 19 arises mainly from the initial position, which can be understood as follows. It comes from the fact that this configuration corresponds to a host atom between two vacancies. Without a vacancy no wind force is experienced. The introduction of a vacancy at position 2 induces a K value of $-25\ \mu\Omega$ cm for the atom at position 1 and, because of symmetry, also for the atom at position 20. An atom feels a force due to the presence of a vacancy in front of it, but also due to a vacancy behind it. If a vacancy is introduced at position 19, atom 1 has both a vacancy in front and behind. If both vacancies could be treated as two separate ones, this would lead to a wind force which is twice as large as the wind force, when only one vacancy is present. As can be seen in Fig. 2 the effect is not that strong, but the fact that it is much larger than in the situation with only one vacancy has now become transparent.

In our calculations the vacancies are treated as if they only change the scattering properties of the environment. However, the addition of vacancies could also change the migration path. When, e.g., an extra vacancy is present at position 3 the atom is likely to jump along a bended path instead of the assumed straight path. This will change the calculated wind valences, especially because the found decrease is mainly due to the additional vacancy. The component of the wind force in the direction of such a bended path, which is indicated in Fig. 3, is calculated and averaged over all equivalent configurations. In the initial position $K=-27.4\ \mu\Omega$ cm comes out, instead of $K=-24.4\ \mu\Omega$ cm for a straight path, so it is somewhat larger. It is not sure how the wind force develops along such a path. In the following we will keep straight migration paths.

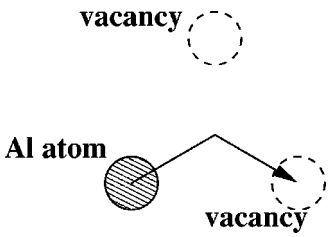

FIG. 3. A migration path bended towards the additional vacancy.

Now we turn to configurations with two additional vacancies in the cluster, of which there are 29 inequivalent. The wind valence varies from $K=-1\ \mu\Omega$ cm for vacancies at the positions 3 and 5 to $K=-46\ \mu\Omega$ cm for vacancies at positions 19 and 20. The average over all configurations is $-30\ \mu\Omega$ cm, which is $4\ \mu\Omega$ cm smaller than for one vacancy. It turns out that the effect of a pair of vacancies on the wind force is found approximately by adding the effects of the separate vacancies. Exceptions are the cases with the vacancies lying close to each other. This is illustrated in Fig. 4, calculated for additional vacancies at the equivalent positions 11, 13, 15, and 17. The difference ΔK of the wind force due to the three different vacancy pairs (11,13), (11,15), and (11,17) with respect to the force for the basic configuration, without additional vacancies, is shown. The solid line gives this difference using twice the effect of one additional vacancy. The curves for the pairs (11,15) and (11,17) follow the solid line closely. For the (11,13) pair, for which the vacancies are close, the effects are much stronger and the sum rule breaks down. Apparently, multiple scattering between the vacancies becomes important.

The wind valence decreases approximately linearly with the increase of the number of vacancies, as shown in Fig. 5. So all the large differences between different configurations with the same number of vacancies are averaged out. The average effect of the addition of one vacancy is about $\Delta K=3.9\ \mu\Omega$ cm. Test calculations show that this trend continues for a larger number of vacancies, although the magnitude

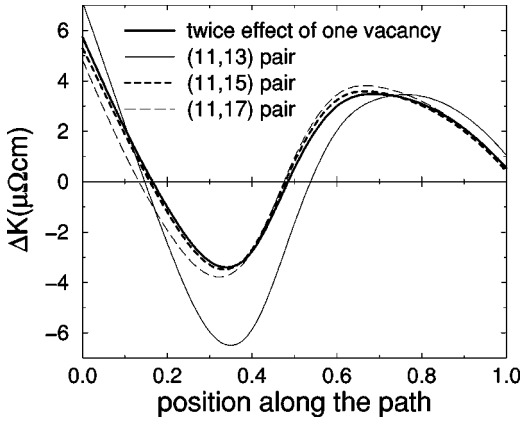

FIG. 4. Difference of K for a jumping host Al atom between configurations with the vacancy pairs (11,13), (11,15), and (11,17) and configurations without additional vacancies. For comparison the sum of this difference due to the separate vacancies is given.

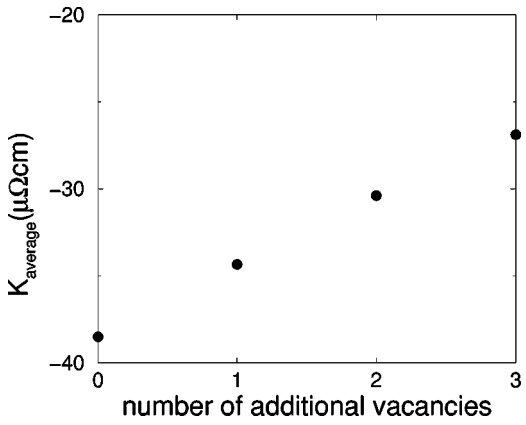

FIG. 5. *K* for a host Al atom, averaged over the path, as a function of the number of vacancies within the cluster.

of the wind valence does not decrease that fast anymore when the number of vacancies exceeds 6.

IV. DISCUSSION

So far only global observations were made in looking at the results. It appears to be worthwhile to develop a more refined view. It was already noticed that the effects depend strongly on the location of the additional vacancies. A large reduction is seen when a vacancy is added at a nearest-neighbor position of both the initial and final positions. Such a position lies in a ring in the plane perpendicular to the migration path at the saddle point and is part of the gate of the four positions 3–6 through which the atom jumps. Especially at the saddle point the reduction of the force is large: namely, a factor of 2. If the vacancy occupies a site farther away, e.g., site 7, the reduction at the saddle point is much smaller: namely, only a few percent. In such cases the force is reduced at the position where the vacancy is nearest. A large increase is observed when the migrating atom moves on a straight line between two vacancies. Then, in the initial position, the force increases by a factor of 1.5, while the average over the entire jump path shows an increase of 7%. The addition of two vacancies implies an enhancement of the effects mentioned. If both vacancies are added to the nearest-neighbor ring of both initial and final positions, the force, averaged over the path, almost vanishes. On the other hand, if a straight line of three vacancies and one jumping atom is considered, the force is raised by 17%, which is approximately the cumulative effect of the case for one additional vacancy considered above. The overall result was already mentioned. An arithmetical average over all configurations shows a reduction of the force by 10% per additional vacancy.

Taking this together, we observe an enhancement of the force if vacancies are lying along the migration path. We are inclined to interprete that as being the trend for the open line shape of a grain boundary. A reduction is observed for vacancies aside the path. Since such vacancies effectively imply a barrier for the migrating atom at one side of the path, one can interpret this as that they simulate a surface. A reduction of the wind force for migration over a surface was indeed found by Bly and Rous.[19]

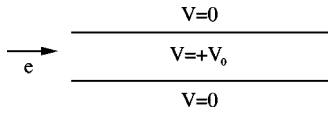

FIG. 6. The jellium metal with a repulsive slab, modeling a grain boundary.

It is worth noticing that the effects from the addition of a vacancy are similar to the effects due to the addition of a Cu atom studied earlier.[11] This can be attributed to multiple-scattering effects, which have been described in detail for a host V atom next to a vacancy.[12] Qualitatively, the scattering current can be divided into two parts. The first and largest part is the Bloch current. This part is not scattered by unperturbed host atoms at lattice positions. Because a host atom next to a vacancy and right before the jump is perturbed by charge transfer, this gives rise to one part of the force. When this atom starts jumping and leaves its lattice position this force increases. This is illustrated by the bold curve in Fig. 2. The second part is only present in the perturbed region, just around the migrating atom, and is the result of scattering. The Bloch current is scattered by a vacancy, which gives rise to circular currents. The resulting current is scattered again by the jumping atom. As already seen for an atom next to a vacancy[12] this current initially points in the direction of the Bloch current, but then it turns and comes back behind the scatterer. The result is similar to the field lines of a dipole. If the jumping atom sees the vacancy in the direction of the current, the wind force is increased, whereas if it sees the vacancy perpendicularly to the current, the wind force is decreased. This relatively simple picture explains qualitatively the results of our calculations.

The fact that the migrating atoms move along grain boundaries has another effect on the wind force. Because of the lower concentration of atoms, electrons are repelled from the grain boundary. Therefore also the current density—and consequently the wind force—is smaller. This effect has been quantified by Sorbello,[8] who calculated the wind force for an atom in a jellium metal. The grain boundary was modeled by a slab with a repulsive potential as shown in Fig. 6. The current density in the grain boundary is expected to be smaller for the assumed direction of the current. The wind force was indeed found to decrease by the same amount as the current density.

V. CONCLUSIONS

The wind force is calculated for a jumping host atom in the vicinity of vacancies. Depending on the distribution of the vacancies, this simulates the open structure at a grain boundary or the absence of atoms at a surface. The vacancies scatter the applied current and thereby change the force on the atom. Our calculations predict an overall decrease of the wind force due to multiple-scattering effects if on the average the jumping atoms see an isotropic distribution of vacancies. For a distribution more typical for a grain boundary the tendency towards an increase of the wind force is found. For

a distribution simulating a surface the decrease found is quite large. These multiple-scattering effects combined with the current reduction effect quantified by Sorbello[8] lead to a fairly complete picture of the processes affecting the wind force at a grain boundary.

For more quantitative predictions it is necessary to extend this study to multiple-scattering effects in realistic grain boundaries. Due to the anisotropy of these effects, a strong dependence on the precise structure of the grain boundary can be expected. This could be done by extending the method of Bly and Rous,[19,20] which can handle systems with two-dimensional translational symmetry already.

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