Monte Carlo Modeling of Thin Film Deposition:

Influence of Grain Boundaries on the Porosity of Barrier Layer Films

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ABSTRACT

We present Monte Carlo simulations of metallic thin films grown by sputter deposition from an infinite target. The Monte Carlo model includes ballistic deposition from the target, surface diffusion, and polycrystalline film growth. We study materials with low atomic mobility such as those involved in "barrier layer" films for silicon devices. We discuss the mechanism leading to columnar growth and the influence of the film orientation on structure and density. Finally, we show that polycrystalline films exhibit voids at the grain boundaries, which leads to columnar growth over a wider range of conditions than that for single crystal films.

Keywords: metal, polycrystalline, barrier layer, Monte Carlo, simulation.

I. INTRODUCTION

Refractory materials (*e.g.* Ti, TiN, Ta, etc) are used in metallization processes to form the interconnects in silicon integrated circuits [1]. Thin films of these materials are used in trenches and vias as liners, in order to avoid diffusion of aluminum or copper into the silicon oxide or silicon. The drawback of using materials having low atomic mobility is the tendency to form low-density films with void networks and rough surfaces. These films exhibit a polycrystalline structure with a preferred out-of-plane orientation but with a variety of grain orientations in-plane. The resulting grain boundaries and void networks provide undesirable channels for diffusion through the barrier layer. Under conditions of high atomic mobility, the films exhibit mainly <111> and <100> textures in fcc materials [2] and <110> and <100> in bcc systems [3].

The aim of this work is to study the effect of grain boundaries on columnar growth and film density. In this paper we describe briefly the main features of ADEPT, our Monte Carlo model (section II). In section III, we discuss the differences between monocrystalline and polycrystalline growth for <111> or <100> textured films using an fcc material with variable atomic mobility. Finally, we summarize our main conclusions in section IV.

II. MODEL

ADEPT is a 3D Monte Carlo model developed to simulate crystal growth of polycrystalline metal films deposited by physical vapor deposition onto a substrate. Here in particular, we are interested in the deposition by sputtering from a target. This model has been described extensively previously (see Ref.[4] for a detailed description), and only a summary of its main features is presented in this section.

A typical simulation is a succession of deposition and surface diffusion events. In the following simulations we assume that the substrate "sees" an infinite target. This implies that the dimensions of the target are large compared to the substrate size, which is the case in industrial Si device processing. Also, we are considering deposition onto a flat surface instead of the interior of a trench. Under these conditions, the deposition of an atom is made by choosing a ballistic trajectory inclined at an angle _ to the normal of the target and a cosine angular distribution. The cosine distribution implies a uniform distribution for the azimuthal angle _, and a *cos*_ distribution for the polar angle. Integrating over _ yields a distribution in _:

$$g(\theta) = A \cdot \sin\theta \cdot \cos\theta \qquad (1)$$

where *A* is a normalization constant.

Next, atomic surface diffusion is described by diffusion coefficients of the form $D=D_0 \cdot \exp(-E_m/kT)$, where the prefactor D_0 and the activation energy for diffusion E_m are coordination dependent. A diffusion hop rate _ is determined for each atom in the film based on its coordination number, $\_=4D/\_^2$, where _ is the hop distance. Then an atom is selected for the diffusion event with a probability proportional to _. Next, potential energies for the initial and final states are calculated using a Monte

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Carlo embedded atom method potential. If the potential energy decreases from the initial to the final state, the event is executed with the rate _. Otherwise the event is executed with a rate _˙*exp(-_U/kT)* where *_U* is the potential energy increase.

Finally, the influence of grain boundaries is modeled by using a single lattice and assigning a grain orientation parameter _ around the surface normal to each atom in the film. A deposited atom will be assigned the same grain orientation as one of its nearest neighbors. An atom is considered to belong to a grain boundary when at least one of its nearest neighbors is in another grain than the one to which it belongs. Two kinds of events are possible for these grain boundary atoms; a reorientation to match that of another crystallite, or a migration event (as described before). The reorientation event is executed with a rate calculated from molecular dynamics [5]. A reduced binding energy is assigned to a bond involving two atoms from a different crystallite. This value is a function of the mismatch angle between the two grains, and is determined from molecular dynamics and experimental results (see Ref.[4]).

III. RESULTS

1. Simulation parameters

Due to the absence of reliable experimental or theoretical parameters (surface diffusion and energetic parameters) for materials like Ta and TiN and in order to carry out a general discussion, we are using a model material with an fcc structure instead. The model is implemented by using the parameters for Al that have been extensively studied by molecular dynamics [4,5] and *ab initio* calculations [6]. To reduce the atomic mobility of aluminum to a range corresponding to refractory materials, the deposition is made at 200K in the simulations, and we re-scale the aluminum diffusion constants by a variable factor $s=D/D_{Al}$ with $10^{-6} \le s \le 1$. The deposition rate is *1_m/min* and in all the simulations 50 monolayers are deposited. The film normal orientation is either [100] or [111]. The substrate is constituted by an atomic layer containing 10^4 atoms with periodic boundary conditions applied in the lateral dimensions.

2. Polycrystalline vs. monocrystalline films

Figures 1(a),(b),(c) are 2D sections of monocrystalline films obtained with different values of the atomic mobility. We chose a [100]-oriented film for the purpose of this discussion. In Fig.1(a) (*s=1*) the film is almost fully dense, few vacancies are visible, and the surface is almost flat. The reduction of atomic mobility (Figs.1(b),(c)) causes the incorporation of vacancies and the formation of columns surrounded by voids. The mechanism of column formation has been extensively studied. Recent molecular dynamics simulations [7] show that columns are formed by the combination of shadowing [8] and low surface mobility. The formation of columns is related to the development of surface roughness (forming surface peaks and depressions).

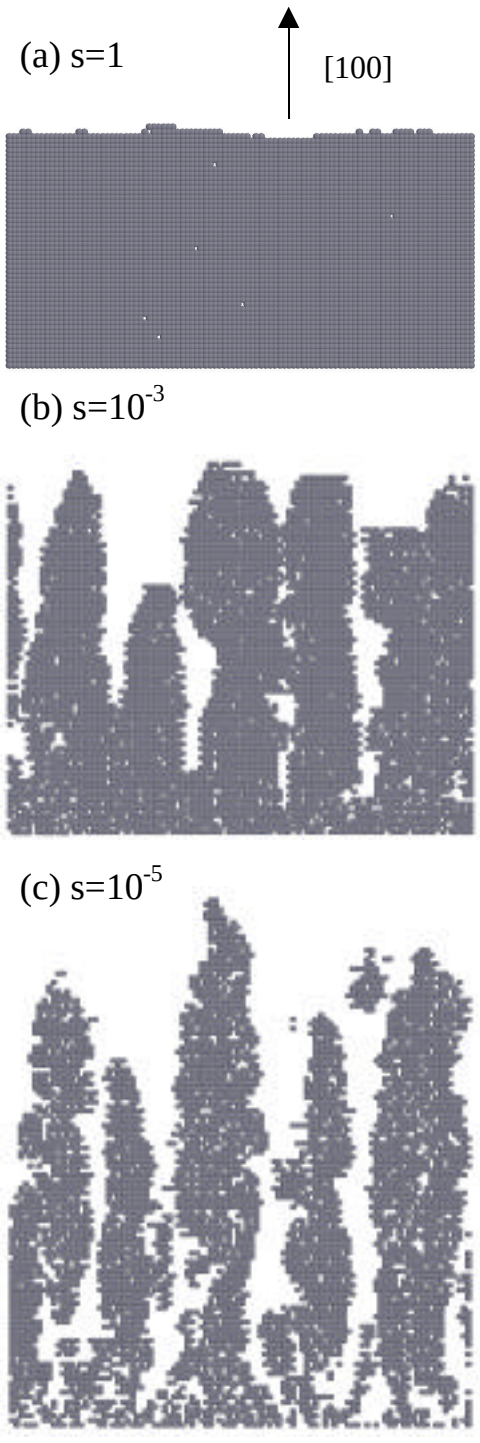

Figure 1: 1 layer thick slice from 3D simulations of monocrystalline [100] oriented films for different diffusion constant ratio *s*.

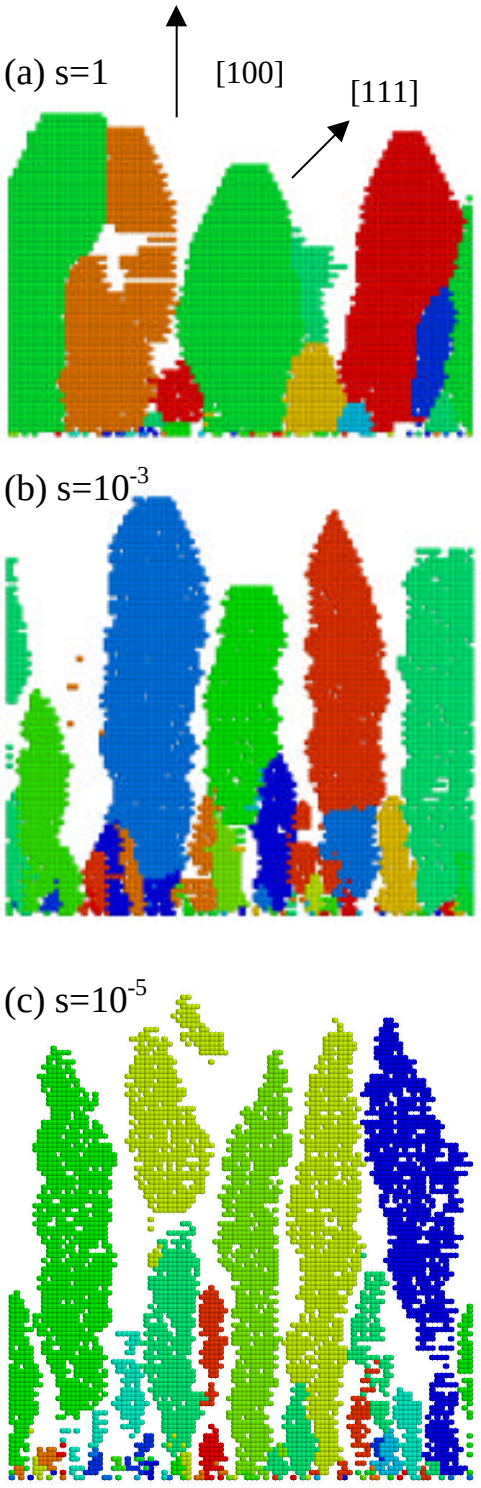

Figure 2: 1 layer thick slice from 3D simulations of polycrystalline [100] oriented films for different diffusion constant ratio *s*. The different colors represent different orientations.

In these simulations atoms are deposited at inclined incidence angles as discussed above with the consequence of shadowing surface depressions from the incoming atomic flux. The low surface mobility prevents atoms from filling up these surface depressions to reduce the surface energy. The same mechanism is involved in our simulations, since the maximum of the angular distribution (Eq.1) corresponds to $\theta = 45^0$, and the atomic mobility is strongly reduced. Nevertheless, the θ distribution allows a disparate set of trajectories from grazing to normal incidence and from any ϕ direction. In contrast, a collimated source emits atoms with approximately parallel trajectories corresponding to the relative positions of the source and the substrate. As a result, complete shadowing of sections of the surface is much more difficult to produce by sputter deposition with a cosine distribution than in an equivalent collimated source emitting at $\theta = 45^0$ [7] with a given ϕ. Columnar growth with a flux obeying a cosine distribution requires a very low atomic mobility. The film thickness is a measure of the density of the film, since the same number of atoms has been deposited in all our simulations. A thicker film is therefore under-dense. Also, the film shows an important decrease of the density as the atomic mobility decreases.

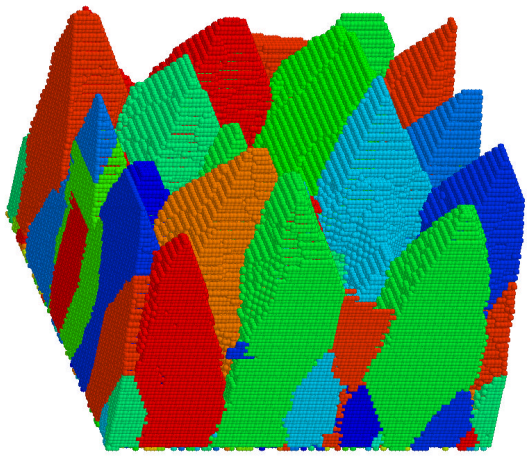

Figure 3: 3D representation of the <100>-oriented polycrystalline film for a diffusion coefficient ratio *s=1*. The different colors represent different orientations.

Films with polycrystalline structure, deposited under identical conditions, are shown in Figures 2(a),(b),(c). In these sections each shade of gray represents a different grain orientation. The morphology of the polycrystalline films can be quite different from the corresponding single crystal films; the grain boundaries lead to lower densities and extend the range of diffusivities that produce columnar morphology. In Figures 2(a),(b),(c), the film consists of grains with voids at their boundaries. In particular,

comparison between Figs.1(a) and 2(a) show an important difference in the film morphology between the single crystal and the polycrystal. The polycrystalline film shows a columnar morphology with the introduction of vacancies and voids at the grain boundaries. Actually, for high atomic mobility, adatoms are able to diffuse from grain boundary to lower energy positions with the introduction of vacancies and voids at the grain interface (Fig.2(a)). The surface roughness is also dramatically modified. Instead of a flat surface, the polycrystalline film exhibit a rough surface with a strong {111} faceting (Fig.2(a)). Figure 3 is the full 3D picture of the film corresponding to figure 2(a), this observation is clearly confirmed for the entire surface. The development of {111} facets is a consequence of the higher growth rate on {100} than on {111} surfaces [4]. Actually, {100} surfaces grow rapidly in heigh but are delimited laterally by {111} facets (Fig.2(a)). As a result {100} facets finally disappear with the formation of sharp columns with {111} facets. We expect grain boundary grooving to initiate this mechanism. In contrast, in Figs.2(b),(c); *i.e.*, for low atomic mobility, the microstructure is similar to the monocrystalline film and does not seem to be influenced significantly by the grain boundaries. The columns are monocrystalline over the entire range of mobilities except for the region close to the substrate.

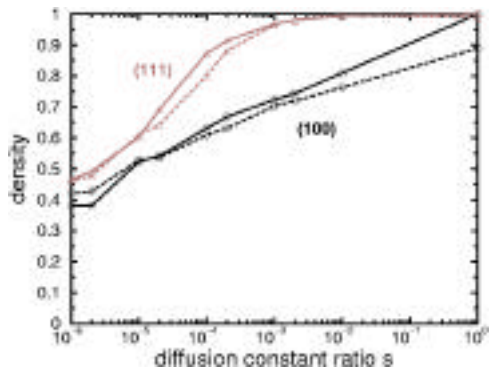

Figure 4: Density of the film averaged between 30th and 40th layers, as a function of the diffusion constant ratio *s*. The black and gray lines correspond respectively to a [100] and a [111] oriented films. Solid lines are the results for monocrystal while dashed lines are the densities for a polycrystalline film.

We have evaluated the variation of film density as a function of film orientation and of the diffusion constant ratio *s*, in polycrystalline and monocrystalline films. For this purpose, we measured the density of a plane by calculating the ratio of occupied sites to the total number of sites in this plane. We averaged these densities between 30th and 40th (100) planes as the mean density is mostly established and the grains are well developed. The results are shown in Fig.4. The monocrystals show a monotonic decrease from a density close to 1($s=1$) to 0.4($s=10^{-6}$) for both (111) and (100). However, a <111> textured film is always denser than <100> for the entire range of *s*, both for the monocrystalline and also in the polycrystalline case. An interesting point in the polycrystalline case is the significant difference between the single crystal and the polycrystalline film for high diffusivity on <100> substrates due to grain boundaries. This effect is not observed on [111]-oriented films because of the very high step energy on these surfaces. Nevertheless this effect might appears for even higher atomic mobility.

IV. CONCLUSIONS

We have presented simulations comparing monocrystalline and polycrystalline films using a Monte Carlo atomic scale simulator. We used model materials with diffusion constants which range from that of Al to refractory materials.

In monocrystalline films, we shown that columnar growth occurs at low mobility. In polycrystalline films, for sufficiently high mobility, we observed columnar growth due to the introduction of voids at the grain boundaries, and this leads to a lower film density than the single crystal film.

Finally, for polycrystalline or monocrystalline films and over the entire range of diffusion constants, <111> oriented films exhibit a higher density than <100> films. Consequently, growth conditions should be chosen in order to favor the close packed texture when depositing films for barrier layer applications.

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