PART I

Fundamentals of Ion-Material Interactions

DYNAMIC MONTE CARLO SIMULATION OF ION BEAM AND PLASMA TECHNIQUES

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ABSTRACT

A multiprojectile version of TRIDYN has been employed to simulate ion-induced effects which occur during ion-beam assisted deposition (IBAD) or plasma-assisted chemical vapour deposition (PECVD) of thin films.

Simulations of the formation of boron nitride films deposited from evaporated boron and energetic nitrogen show an excellent agreement with experimental results for nitrogen concentrations below the stoichiometric limit. For high N/B flux ratios, non-collisional mechanisms (ion-induced outdiffusion, surface trapping of outdiffusing nitrogen) have been included in the simulations, again producing good agreement with the experimental results.

Simulations of the PECVD of hydrocarbon films suffer from the poor knowledge of the neutral and ionic fluxes which contribute to the growth of the layers. Nevertheless, the composition of the films and its dependence on ion energy can be predicted with satisfactory agreement with experimental findings. A simple model of preferential displacement yields a reasonable average ratio of sp^2 and sp^3 coordinated carbon atoms. The energy dependence of the bond ratio is in contradiction to experimental observation.

INTRODUCTION

Ion irradiation effects are known to play an important role for the growth and properties of thin films being deposited by the assistance of ion beams or plasmas[1-5]. Although numerous phenomenological studies are available and some qualitative understanding has been achieved, the quantitative modelling of ion bombardment effects is still at an early stage. Ions may act on a growing film physically through collisional effects like implantation, sputtering, atomic relocation or radiation damage. In addition, ions might promote chemical reactions at the surface or in the bulk, or they might enhance diffusion or precipitation. For the purpose of quantitative modelling, sufficient basic knowledge is only available for the collisional effects. Thereby, first model calculations will apply to systems in which mainly physical mechanisms control the growth rate and determine the film properties.

Recently, Carter et al.[6] published an analytical altered layer model for the growth of thin films under the influence of atomic relocation and sputtering. Very simplistic analytical expressions, taking only into account the reflection of the energetic component and the sputtering of the thermal component, have been given by Hubler and VanVechten et al. for the IBAD of nitrides[7,8]. The evaluation of the analytical predictions requires data for, e.g., ion reflection or sputtering which are conveniently taken from static binary collision approximation (BCA) computer simulation[9]. The results of such simulations may alternatively be inserted into rate equations governing the layer growth. Such an approach has been chosen by Müller[10] in order to treat the ion-induced densification of oxide films. As a further possibility, static BCA simulations can be performed stepwise with intermediate deposition of the thermal component. Zhou et al.[11] used this approach for the IBAD of silicon nitride.

In the most direct way, BCA computer simulation can be applied to the film growth and composition in the form of a fully dynamic simulation which covers ion and neutral deposition, ion reflection, sputtering and atomic relocation simultaneously, thus avoiding any further simplification in addition to the restriction to collisional mechanisms. The present paper will give a short description of the TRIDYN code, and show some results in comparison to experimental data for the IBAD of boron nitride and the PECVD of amorphous hydrocarbon films.

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COMPUTER MODEL

For the model calculations to be described below, a modified version (4.0)[12] of the TRIDYN programme[13,14] has been employed. TRIDYN is based on the multicomponent, sputtering version[15] of the well-known TRIM[16] code. The present version treats up to five different species of incident atoms simultaneously.

An extensive description of the code has been given in Ref.14. Briefly, the species of incident (thermal or energetic) atoms is chosen by means of a random generator according to the composition of the incident flux. In case of molecular ions, the total energy is distributed over the atomic constituents according to their masses. The substance is subdivided into thin slabs of app. 2 Å thickness. The histories of incident projectiles and knock-on cascade atoms are traced as sequences of free-flight paths and elastic binary collisions in an universal averaged screened Coulomb potential (the 'Krypton-Carbon' potential[17]). The inelastic energy loss to the electrons is composed with equal probability from nonlocal (Lindhard-Scharff[18]) and local (Oen-Robinson[19]) interaction.

A planar potential is adopted for the binding of surface atoms. The sputtering yields are determined critically by the choice of the surface binding energies, which are given below for the specific examples. The cutoff energies at which the particle histories are terminated are set equal to the surface binding energies.

The dynamic alteration of the substance is accomplished by a local relaxation of each depth interval according to a density given by the local composition[13]. The atomic volumes of the constituents of a two-atomic substance are usually chosen in such a way that the densities of one pure component (e.g. boron in the case of B:N) and a stoichiometric compound (BN) result correctly.

Each incident pseudoatom in the simulation represents around 10^{12} projectiles/cm^2. Thereby, a simulation for a total fluence of the order of 10^{17}/cm^2 requires about 10^5 pseudoprojectiles. Typical computing times were between 1 min and 50 min on a CRAY XMP computer, depending on the ion energy.

RESULTS AND DISCUSSION

Ion-Beam Assisted Evaporation of B:N

A thorough experimental study on the ion-assisted formation of B:N films has been performed by Burat et al.[20]. The films were prepared by simultaneous boron evaporation and N_2^+ bombardment at energies between 250 eV and 2 keV, with ion-to-neutral flux ratios between 0.3 and 2. The results include high-energy ion beam analysis of the bulk composition, Auger electron analysis of the surface composition and sputtering and incorporation measurements for nitrogen and boron.

Corresponding simulation runs were performed with TRIDYN, starting with a pure silver substrate. For the surface binding energies of B and Ag, their enthalpies of sublimation (5.7 eV and 2.97 eV, respectively) were chosen. For nitrogen, the surface binding energy of 6.32 eV is consistent with the heat of fusion of BN and the dissociation enthalpy of N_2.

The compositional depth profile of such a simulated film is shown in Fig.1 for a grown thickness of about 120 Å. The interface to the silver substrate shows an intimate mixing due to nitrogen implantation and atomic mixing. For boron, a stationary bulk concentration is not yet fully developed for the given fluence, in contrast to nitrogen. Due to subplantation of the energetic nitrogen behind the evaporated boron, the surface is always enriched with boron. The simulated bulk concentrations as well as the boron and nitrogen incorporations are in excellent agreement with the experimental data for nitrogen energies between 125 and 1000 eV/atom, as long as the bulk composition stays below or close to the stochiometric composition of N:B = 1:1[12]. However, at N/B flux ratios above 1:1 the predicted nitrogen incorporation becomes excessively high compared to the experimental findings.

The good agreement between computer simulation and experiments indicates that

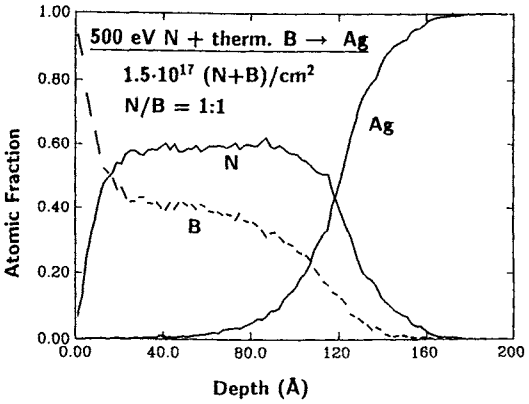

Fig.1:
Compositional profile of a B:N film and the film/substrate interface during IBAD deposition, as obtained from a TRIDYN computer simulation. The nitrogen ions are incident at an angle of 30^0 with respect to the surface normal. The ion-to-neutral flux ratio is 1:1.

the growth and the composition of the films with sufficiently low nitrogen concentration can be well described by collisional effects only. For high ion-to-neutral flux ratios which would result in a hyperstoichiometric nitrogen concentration, some kind of an ion-induced outdiffusion of excess nitrogen atoms, the detailed mechanism of which is unknown, will limit the nitrogen concentration. This is corroborated by the finding that the nitrogen surface concentration observed in experiments with high N/B flux ratios, is larger than predicted by the simulation, indicating a surface nitridation by outdiffusing nitrogen atoms.

In extended simulation runs, ion-induced release has been included for excess nitrogen (i.e., nitrogen above the stoichiometric concentration). From each depth interval within the ion range, nitrogen atoms are removed with a rate being proportional to the local excess concentration. In addition, released nitrogen atoms were allowed to become trapped at the surface with a given probability. Both the release rate and the surface trapping probability have been varied in order to obtain best fits to the experimental data. Fig.2 demonstrates an excellent reproduction of the experimental results when both release and surface trapping are included.

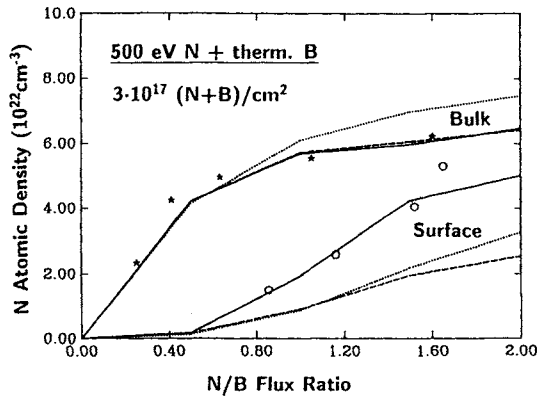

Fig.2:
Bulk (full symbols, upper three lines) and surface (open circles, lower lines) nitrogen density in an IBAD B:N film, for different ion-to-neutral flux ratios. Symbols represent experimental data from Ref.20, lines are from TRIDYN simulations with collisional processes only (dotted), including local release of nitrogen above the stoichiometric limit with a fitted rate constant (dashed), and including local release and surface trapping of released nitrogen with a probability of 0.5 (solid).

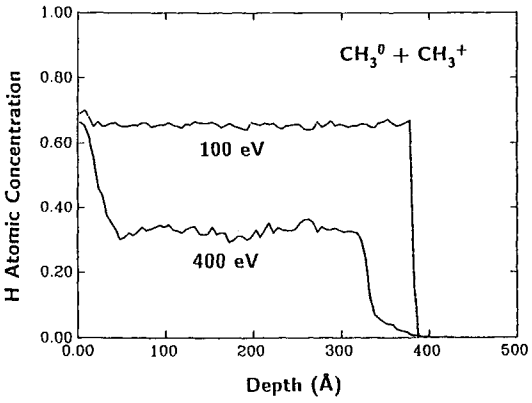

Fig.3:
Hydrogen depth profiles in C:H films deposited on silicon, from TRIDYN simulations. The films are modelled to grow from neutral and ionic methyl radicals with an ion-to-neutral ratio of 1:9, at two different ion energies. The simulations include collisional ion-induced release of hydrogen (see text).

Plasma Assisted Deposition of C:H Films

Generally, the modelling of ion bombardment effects during plasma assisted deposition is subject to larger uncertainties than for ion-beam assisted deposition, since the neutral and ionic species which contribute to the film growth are mostly unidentified, and their fluxes are generally unknown. A relatively simple system for which ion bombardment effects turn out to be significant is the plasma-enhanced deposition of C:H films from hydrocarbon gases[21–23]. For a methane plasma, the CH_3 radical is probably the main species contributing to the layer growth (Ref.24 and references therein). A typical hard a-C:H film contains about 0.4 hydrogen atoms per carbon atom. Therefore, a hydrogen depletion must occur during film growth.

The TRIDYN simulation assumes that this depletion is mainly due to ion-induced effects. Experiments with a-C:H layers generated by keV hydrogen implantation into graphite[25] suggest that hydrogen can be knocked off its binding site by the interaction with fast atoms. Subsequently, such free hydrogen atoms will recombine to molecules which will quickly outdiffuse through the surface around or above room temperature. For the present simulations, it is assumed that the rate-controlling step is given by the knockoff. A hydrogen atom will be released after receiving an energy transfer larger than an average C-H binding energy (2.5 eV) either through elastic energy transfer during collisions or due to electronic interaction. Rather arbitrarily, a release efficiency of 0.5 has been assumed for nuclear and electronic interaction[24]. The surface binding energies for C and H have been chosen as 4.5 eV, with negligible influence on the results since the sputter yields are sufficiently small.

A reasonable assumption for typical RF plasma deposition conditions is a 10% ionic fraction of the impinging hydrocarbon flux[24]. CH_3^+ is chosen as a model ion for the simulations. A typical result is shown in Fig.3 for two different ion energies. Significant interface mixing is only observed for the higher ion energy of 400 eV, being in good quantitative agreement with experimental results obtained from sputter profiling[26]. The bulk concentration of hydrogen is also in good agreement with experimental experience. At an ion energy of 400 eV, an atomic ratio of about 35% is predicted which is typical for a hard a-C:H film, whereas a low energy results in a polymer-like film with a high hydrogen concentration. However, these results should be considered merely qualitatively in view of the above assumptions and simplifications. The simulation also predicts hydrogen enrichment at the surface, which has also been confirmed experimentally[27].

The optical, mechanical and electrical properties of C:H films are determined both by their hydrogen content and their bonding structure. The films are considered to mainly consist of an amorphous network of graphitic islands with sp^2 bonds which are interconnected by diamond-like sp^3 bonds. For the formation of either sp^2 or sp^3 bonds during film growth, a preferential displacement model has been proposed qualitatively[28–30] which accounts for the different displacement thresholds of sp^2 coordinated carbon atoms (25 eV

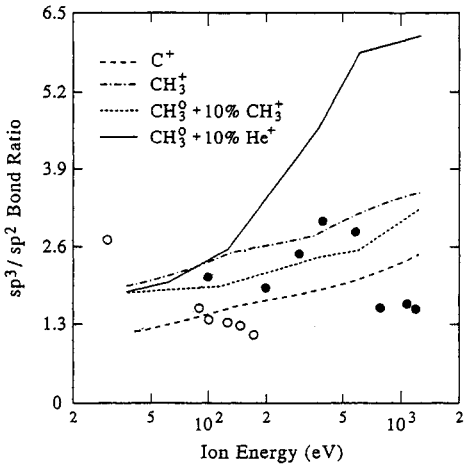

Fig.4:
Ratio of diamond-like and graphite like carbon bonds in mass-selected ion beam or plasma-deposited C:H films versus ion energy, for different ionic and neutral species. Lines are from TRIDYN simulations including a simple preferential displacement model (see text). Experimental data are shown for comparison, which have been obtained from infrared absorption after methane plasma deposition (Ref.31, full points, abscissa denotes self-bias voltage), and from nuclear magnetic resonance after acetylene plasma deposition (Ref.32, open circles, abscissa denotes measured mean ion energies).

in graphite) and sp^3 carbon (80 eV in diamond). TRIDYN simulations have been performed in order to quantify this proposal. It is assumed that carbon atoms are released from their sites at elastic energy transfers above their displacement thresholds. Both implanted and released atoms are fed into the sp^2 or sp^3 populations with equal probability.

Results are shown in Fig.4 for different species which impinge during mass-selected ion beam deposition or plasma deposition, together with some experimental data[31,32]. A rather good agreement between experiment and model prediction is observed for the average bond ratio in the present range of ion energies. However, discrepancies are found for the energy dependence: Whereas the predicted bond ratio steadily increases at increasing ion energy, the experiments reveal a decrease towards high energy. (It should be noted that the results of Refs. 31 and 32 are not necessarily in contradiction, as infrared absorption[31] only probes hydrogenated carbon atoms.) A clear increase of sp^2 bonds at high energy is also confirmed by recent detailed NMR studies performed after methane plasma deposition[33]. From this, one may conclude that the present simple model of preferential displacement alone is not sufficient to describe the bond ratio in amorphous hydrogenated carbon films.

CONCLUSIONS

It has been demonstrated in the present paper that dynamic computer simulations based on the binary collision approximation may be of great help for the understanding of ion bombardment effects during thin film growth. The existence of systems which are mainly governed by collisional effects has been proven. It is also possible to include a simple modelling of other than collisional mechanisms such as ion-induced release or atomic trapping.

Especially for plasma deposition, the capability of the simulations is hampered by the poor knowledge of the boundary conditions such as ion and neutral fluxes and energies. It is desirable that the availability of simulations of the present type would trigger an increased activity in performing well-characterized experiments correlating the impinging species and the properties of the resulting films.

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SIMULATIONS OF LOW-ENERGY ION/SURFACE INTERACTION EFFECTS DURING EPITAXIAL FILM GROWTH.

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ABSTRACT

Molecular dynamics simulations were used to follow low-energy ion/surface interactions including kinetic energy redistribution in the lattice as a function of time, projectile and lattice atom trajectories, and the nature, number, and depth of residual defects. The simulations were carried out using the Tersoff many-body potential for Si. Irradiation events were initiated with 10 and 50 eV Si atoms incident normal to the Si(001)2x1 surface at an array of points in the primitive surface unit cell. Ion-induced epitaxial growth was observed due to both Si projectiles and Si lattice atoms coming to rest at epitaxial positions through direct deposition as well as site exchange occurring via diffusional and collisional processes. 36 simulations of 10 eV (50 eV) Si bombardment resulted in an average stopping position of 0.5 Å (1.6 Å) below the surface, 10 (13) epitaxial events, 7 (24) exchange events between the projectile and a lattice atom, and the formation of 15 (63) interstitials and 0 (36) vacancies. The interstitials preferentially diffuse toward the surface and are annealed out over times corresponding to monolayer deposition at typical Si MBE growth temperatures.

1. Introduction

There is a general trend in thin-film processing technologies towards kinetically-limited rather than near-equilibrium deposition processes. One of the primary approach being explored involves the use of low-energy (typically ≤ 200 eV) ion bombardment during deposition. Low-energy ion/surface interactions can be used for controllably modifying microstructure and/or microchemistry during vapor-phase crystal growth by a variety of techniques including plasma-assisted chemical vapor deposition, sputter deposition, primary-ion deposition, and ion-assisted molecular-beam epitaxy (MBE)[1].Useful effects including film densification[2,3], preferred orientation in polycrystalline films [4,5], decreased epitaxial temperatures [6-8], increased elemental incorporation probabilities [9,10], more abrupt doping profiles [10], and growth of new metastable phases [11-13] have been demonstrated. Enhanced adatom mobilities [14], changes in nucleation kinetics [15], collisionally induced dissociative chemisorption [16], dissociation of incipient islands during nucleation [15,17], and trapping in near-surface sites [9,10] have been reported as benefits of low-energy ion irradiation.

For example, several groups have demonstrated reduced epitaxial temperatures during Si MBE experiments in which a fraction of the incident condensing beam is ionized and accelerated to energies Ei < 200 eV[6,8,18]. In addition, low-energy accelerated ion doping during Si MBE experiments has been shown to overcome problems associated with low dopant incorporation probabilities σ and surface segregation [9,10]. Dopant incorporation probabilities were increased by more than 5 orders of magnitude over those obtainable by coevaporative doping and doping profiles were extremely abrupt. Using optimum ion energies E_i and elevated substrate temperature T_s, ion-doped MBE Si films have exhibited excellent electrical and optical properties

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without measurable (detection limit ≈ 10^{12} cm^{-3}) electrically-active defects as determined by temperature-dependent Hall measurements [19], deep-level transient spectroscopy [20], and photoluminescence [20] in the case of In^+ (E_i=200eV, T_s=800°C) and As^+(E_i=200eV,T_s≥600°C).

Mechanisms such as trapping and changes in surface segregation kinetics, preferential sputtering, collisional mixing, and ion-stimulated desorption have been used to interpret and model these effects [1]. Models based upon continuum analytical approaches [10,21] or Monte Carlo simulations [3,22] have been successful in explaining general features of observed experimental results described above, but they are inherently incapable of probing the details of individual ion/surface interactions for which molecular dynamics (MD) simulations are well suited.

In this paper, we present results obtained using molecular dynamics (MD) to investigate ion/surface interaction mechanisms which control the kinetics of the MBE Si growth. Specifically, we have used the MD simulations to follow the trajectories of individual incoming projectiles and lattice atoms following irradiation events initiated at an array of points in the primitive unit cell of a reconstructed Si(001)2x1 surface[23,24]. Bombardment-induced epitaxy, formation of the defects including interstitials and vacancies are discussed.

Collisional sequences resulting from ≤100eV Si irradiation are essentially complete within ≈1ps, which correspond to ≈15 cycles for a Si zone-center optical phonon with a period of 63.8 fs. The lattice atoms involved in the collision cascade attain kinetic energies (>0.5eV), corresponding to temperatures well above those used during typical MBE Si growth experiments (500 - 800 °C). Because of the extreme differences in the time scales as well as atomic kinetic energies associated with the creation and annealing of collisionally-induced defects, we have treated these two cases separately. We chose the starting temperature T_s=0K for the collision simulations. Condition of T_s=0K makes each collisional events and trajectories simple and understandable[23]. The temperature effects such as annihilation and diffusion of defects were discussed by calculating the activation energies of the atomic migrations[25].

2. Simulation Procedure

The simulations were carried out using the Tersoff many-body empirical potential which has been shown to provide a good description of energies and bond length in diamond-structure Si and its polytypes, elastic properties, point defects, and the Si(001)2x1 surface reconstruction[26].

The forces during each time step of the MD calculations were defined in terms of the gradient of the potential energy with respect to the length of the vector connecting each pair of atoms and the angle between pair of vectors. The positions and velocities of every atom in the computational cell were calculated following each time step by integrating the equations of motion using the Schofield algorithm [27] which is a simple, stable, and low-order integration routine that requires force calculation once for each time step.

The atomic position relaxation including the stable atomic configurations of defects and surface reconstruction as well as the final stable atomic configurations after the bombardments were investigated using quasidynamic (QD) simulations[28]. The potential energies and forces associated with each atoms in the computational cell, as well as the total potential energy and maximum force value, were calculated for each time step and atomic configurations were allowed to relax in the QD simulations. The position and velocities of each atom were computed in a fully dynamic mode until both the total potential energy and the total force of the ensemble (independently) reached minima at which point the velocity of each atom was set to zero and the system allowed to evolve further. The procedure was repeated until stable atom positions, with approximately zero net force (≤2x10^{-4}eVÅ^{-1} ≈3x10^{-8} dyn), were obtained. The initial time steps