Differential sputter yields in $Si_{1-x}Ge_x$

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Sputter yields for ion bombardment of $Si_{1-x}Ge_x$ alloys are computed using molecular dynamics simulations with the target material modeled using the Stillinger–Weber empirical potential. The results show that Si atoms are preferentially sputtered relative to Ge atoms for all x. The parameters of the Stillinger–Weber potential are altered to investigate the relative importance of atomic mass, bonding energy, atomic number, and atomic density leading to the observed differential sputter yields. The results explain an experimentally observed nonlinear dependence of total sputter yields on composition in $Si_{1-x}Ge_x$ [Tuboltsev *et al.*, Phys. Rev. B **72**, 205434 (2005)]. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2896451]

INTRODUCTION

Ion bombardment of semiconductors is known to remove substrate mass by sputtering and is used for depth profiling of polycrystalline multilayers[1–3] and in other applications. Sputtering has also been proposed as the mechanism causing ripples to form on the bombarded surfaces under certain conditions.[4,5] The differential sputtering of the constituents of multicomponent and alloy surfaces offers the possibility of enriching one component on the surface or even growing nanostructures rich in one of the components making up the target material. It has been observed in Si–Ge systems that composition affects net sputter yield in a complex fashion,[6] but it has not been possible to measure the relative amount to determine the so-called preferentiality of Si versus Ge sputtering in this system. The net sputter yield, for example, for $Si_{1-x}Ge_x$ targets is seen to have a nonlinear dependence upon x, but the ratio of Si or Ge sputtering is not known.

Recently, the difference in sputter yields of constituent atoms in $Si_{1-x}Ge_x$ has been speculated to be a potential reason for observed modulations of ripple composition.[4] But in an explanation proposed in that effort, the sputter yields of constituents are assumed to be the same as those from pure targets, so any composition dependence of sputter yields is neglected. Evaluating this approximation and understanding Si and Ge contributions to the net sputter yield of $Si_{1-x}Ge_x$ are the objectives of the present simulations.

For single-species targets, it is thought that sputter yield depends upon the relative atomic masses of the incident ions and the substrate, their relative atomic numbers, and the atomic number density and bonding energy of the target material. These, of course, are not all independent parameters, which makes interpreting the root cause of experimental observations challenging. Atomic number was used by Wittmaack[7] to discuss sputtering of Si targets by 1 keV impact ions. It was found that sputtering was insensitive to the atomic number ratio between projectile atom and the target atoms, Z_P/Z_t, for $1.05 \leq Z_P/Z_t \leq 1.25$ but significantly more sensitive to it for $Z_P/Z_t < 1$. Similar behavior is observed for mass ratio variation,[7] with Si sputter yield varying inversely with the mass of the projectile isotope for $Z_P/Z_t > 1$, but not for $Z_P/Z_t < 1$. In a study designed to specifically study the mass dependence of sputter yield, Ge isotopes were bombarded with Ar^+ ions. In this case, a slight increase in sputtering for lighter Ge isotopes was observed.[8]

Simulations are well suited to independently adjust the system parameters to understand these individual effects. This approach was used by Shulga,[9] who varied the properties of Si individually, calling it pseudo-Si. Under bombardment with Ar^+ ions, they found that the angular distribution of sputtered atoms is more sensitive to mass and atomic number than number density and bonding in the target. We take a similar approach to study the differential sputter yield of $Si_{1-x}Ge_x$.

METHODOLOGY

The simulation domain, as shown schematically in Fig. 1, is constructed with 10 unit cells of equilibrium lattice constant $a_x = [a_{Si}(1-x) + a_{Ge}x]$ in each of the three coordinate directions. Here, a_{Si}, and a_{Ge} are equilibrium lattice constants

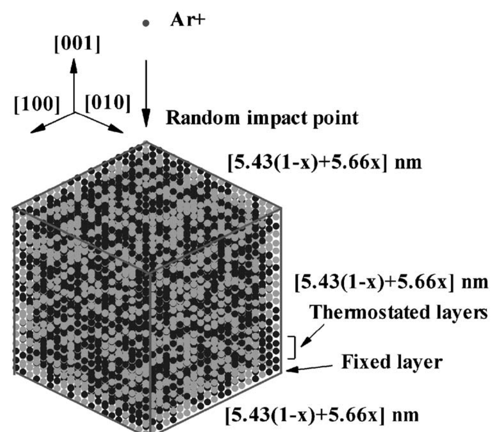

FIG. 1. The simulation domain for $Si_{0.5}Ge_{0.5}$.

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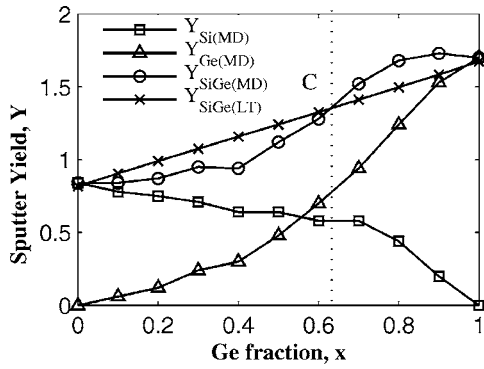

FIG. 2. Total sputter yield and individual sputter yield as a function of Ge content in the target. MD represents our results and LT represents the Sigmund's linear cascade theory estimation.

for Si and Ge, respectively. In our study, the Ge fraction x is varied from $x=0.0$ to $x=1.0$ with intervals of $\delta x=0.1$. The target surface normal is taken as the [001] direction. Periodic boundary conditions are enforced in both the [010] and [100] directions. The locations of the Si and Ge atoms in the lattice are randomly chosen within the domain and relaxed using a conjugate gradient method before the simulation begins. The system is integrated in time with the velocity-Verlet algorithm with time step $\Delta t=0.15$ fs, which is sufficient to track atomic interactions accurately after an impact.[10]

Atomic interactions between the target atoms (Si–Si, Si–Ge, or Ge–Ge) are modeled by the Stillinger–Weber potential[11] with parameters chosen from Refs. 11 and 12 for Si and Ge, respectively. The Moliere potential[13] is used for interactions between target atoms and projectile atoms (Ar–Si or Ar–Ge). Composition effects on the lattice constant and Stillinger–Weber parameters for Si–Ge interactions are taken as arithmetic averages of the parameters for the constituent atoms.

In the initial stage of the simulation, before any bombardment, a Berendsen thermostat[14] is applied to all atoms to equilibrate the target to 77 K. Then the Ar^+ ion is directed normal to the surface at a random position with energy of 1 keV. The impact heats the target; to model cooling due to conduction into the bulk after an impact, the thermostat is applied only to the bottom two unit cells.

Atoms are observed to sputter only within 15 000 time steps (2.25 ps) after the impact. Hence, at this time after the atom hits the target, sputtered atoms are identified as those that leave the surface and cross a plane 1.5 nm above the top surface. For each choice of x, results have been calculated as arithmetic average over 100 realizations. No significant variation was observed with averaging additional cases.

RESULTS AND DISCUSSION

Sputter yield is defined as the average number of sputtered atoms per ion impact. In our simulation, sputter yields of pure Si and Ge are found to be 0.84 and 1.70, respectively, which agrees reasonably well with experimental measurements 0.93 (Ref. 15) and 1.52.[16] The total sputter yield for $Si_{1-x}Ge_x(Y_{SiGe})$ as well as sputter yields for its components Y_{Si} and Y_{Ge} are shown in Fig. 2.

Total sputter yields are compared with values predicted by Sigmund's linear cascade theory,[17] for which the total yield is predicted to be proportional to x. In Fig. 2, this can be seen as the straight line between the pure Si and pure Ge sputtering rates. In using this linear cascade theory, the target is assumed to be a single-component target with atomic number, atomic mass, and bonding energy obtained by weighting averages over the constituent atom. Unlike this linear prediction, all the computed sputter yields, Y_{SiGe}, Y_{Si}, and Y_{Ge}, vary nonlinearly with composition. Y_{SiGe} matches with linear cascade theory estimation at $x=0.63$, which we define as the crossover composition shown as "C" in Fig. 2. For $x\leqslant 0.63$, Y_{SiGe} is less than the linear theory estimation whereas it exceeds the linear theory for $x\geqslant 0.63$. Tuboltsev *et al.*[6] observed a similar trend experimentally for bombardment of $Si_{1-x}Ge_x$ with 3 KeV Ar^+ ions.

Individual sputter yields show different behavior as the species content varies in the compound target. For $x>0.63$ both Y_{Si} and Y_{Ge} are more strongly dependent upon x than for $x<0.63$. It appears that the biasing of the crossover point away from $x=0.5$ toward $x=1$ is related to the disparate response for small amounts of Ge versus small amounts of Si. That is, small changes in Ge content in a Si-rich alloy affect the sputter yields (total and of individual components) significantly less than small changes in Si content in a Ge-rich alloy.

Sputter preferentiality, δ is defined as

$$\delta=\frac{Y_{Ge}C_{Si}}{Y_{Si}C_{Ge}}-1=\frac{(1-x)Y_{Ge}}{xY_{Si}}-1. \qquad (1)$$

Here, Y_k and C_k are partial sputter yields and equilibrium surface concentration, respectively. A commonly used analytical form for sputter preference is Sigmund's expression,[18,19]

$$\delta=\left(\frac{M_{Si}}{M_{Ge}}\right)^{2m}\left(\frac{U_{Ge}}{U_{Si}}\right)^{1-2m}-1, \qquad (2)$$

where M_k and U_k ($k=\mathrm{Si},\mathrm{Ge}$) are atomic mass and surface binding energy, respectively. For sputtering, the value of the empirical parameter m is typically assumed to be in the range $0\leqslant m\leqslant 0.2$,[18–20] an assumption that we investigate for Si_xGe_{1-x} by computing the effective m from our molecular dynamics (MD) data. From Eq. (2), m is

$$m(x)=\frac{1}{2}\frac{\ln\left[\frac{(1-x)Y_{Ge}U_{Ge}}{xY_{Si}U_{Si}}\right]}{\ln\left[\frac{M_{Si}U_{Ge}}{M_{Ge}U_{Si}}\right]}. \qquad (3)$$

Taking atomic mass ratio, $M_{Si}/M_{Ge}=0.3888$, and binding energy ratio, $U_{Si}/U_{Ge}=1.2113$, the composition dependence of "m" and "δ" are calculated using our individual sputter yield information. Results are plotted in Figs. 3 and 4 for preferentiality δ and parameter m, respectively.

It is found that m varies by only about a factor of about 2, $0.13<m<0.27$, and δ varies more, with $-0.40\leqslant\delta\leqslant -0.10$. The negative values indicate that over the entire composition range, Si shows a small sputter preferentiality to Ge,

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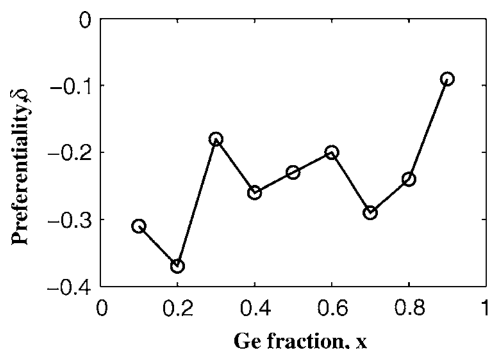

FIG. 3. Preferentiality δ as a function of Ge content.

though the trend diminishes as Ge fraction increases. This has not previously been reported for $Si_{1-x}Ge_x$.

To understand the physical properties of the materials that lead to sputtering preference we separately consider the effects of mass (M), atomic number (Z), bonding energy (U), and atomic density (N) for each species of the target. We do this by substituting one or two of the parameters defining the target species (Si or Ge) interaction potential with the corresponding property from the other species. We denote these pseudo-Si and pseudo-Ge atoms by Si* and Ge*. For comparison, similar calculations are performed with linear cascade theory and SRIM-2003,[21] for the same adjustments of the physical parameters.

The resulting molecular dynamics sputter yields in Table I show that Si sputter yields are more sensitive to changes in mass, atomic number, bonding energy, and atomic density than Ge sputter yields. The sputter preferentiality, Fig. 3, showed the preference of Si sputtering over Ge. This could be attributed to the higher sputter yield sensitivity of Si. Furthermore, the individual effects show atomic density to be the most significant parameter for Ge, and mass or bonding energy for Si. Combined mass and atomic number for both Si and Ge shows a significant effect on sputter yields compared to either bonding energy or mass alone. The tabulated data also show that sputter yield increases with increasing mass and atomic number, combined, and with atomic density, but that it is inversely related to bonding energy. Among the effects, both for Si and Ge, the effects of combined mass and atomic number, and atomic density are seen to be more important than the inverse effect of bonding energy. Hence, attributing the observed nonlinearity to the nearest-neighbor configuration specific bonding energy alone as proposed by Tuboltsev *et al.*,[6] without consideration of mass and atomic number, is incomplete in view of the present results. Rather, the combined effects of effective mass and atomic number appear to be more important.

SRIM results are significantly different from linear theory predictions and MD calculations. The discrepancy could be attributed to the error in SRIM sputter yield results as a function of atomic number ratios.[7]

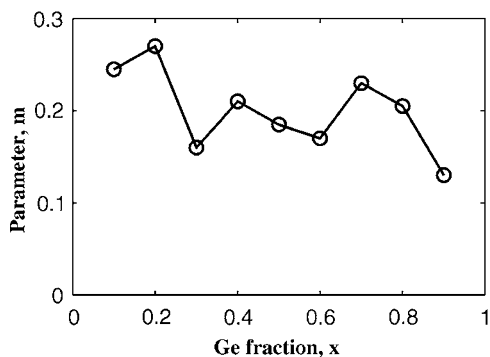

FIG. 4. Parameter m as a function of Ge content.

TABLE I. Sputter yields of (a) Si and Si* (b) Ge and Ge* for the molecular dynamics simulations (MD). For comparison, results based on the linear cascade theory (LT) of Sigmund (Ref. 17), and SRIM-2003 (Ref. 21), are presented. Experimental sputtering yields are obtained from Refs. 10 and 11 for Si and Ge, respectively.

	Si	Si*				
		(M_{Ge}, Z_{Ge})	M_{Ge}	Z_{Ge}	U_{Ge}	N_{Ge}
MD	0.84	2.15	1.27	1.22	1.26	0.79
Expt.	0.93	⋯	⋯	⋯	⋯	⋯
LT	0.83	1.30	0.94	1.12	1.00	⋯
SRIM	0.76	1.70	⋯	⋯	0.93	0.70
	Ge	Ge*				
		(M_{Si}, Z_{Si})	M_{Si}	Z_{Si}	U_{Si}	N_{Si}
MD	1.70	0.94	1.64	1.59	1.62	2.12
Expt.	1.52	⋯	⋯	⋯	⋯	⋯
LT	1.67	1.00	1.36	1.17	1.34	⋯
SRIM	1.89	0.84	⋯	⋯	1.54	2.12

CONCLUSIONS

We report complete differential sputter yield information for $Si_{1-x}Ge_x$ under 1 keV Ar^+ ion bombardment, obtained by molecular dynamics simulation. The empirical parameter m, related to differential sputter yield, is found to fall within a narrow range. It is seen that Si is preferentially sputtered over Ge for the entire composition range of Ge in $Si_{1-x}Ge_x$. A pseudoatom MD analysis shows that the combined effect of atomic mass and atomic number is important in explaining the nonlinearity of total sputter yields.

ACKNOWLEDGMENTS

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