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THE ROLE OF THERMODYNAMIC PHASE DIAGRAMS AND LATTICE MATCHING IN SUPERLATTICE GROWTH

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Metallic superlattices exhibit a correlation between the epitaxial growth temperature and temperatures extracted from the equilibrium thermodynamic phase diagram. This correlation together with molecular dynamics simulation of epitaxial growth indicates that thermodynamics plays an important role in the growth of epitaxial films, particularly in limiting the sharpness of the interfaces.

The growth of semiconductor and metal superlattices has been a subject of considerable interest for a number of years.¹⁻³ This is motivated by the novel physics and material science that can be studied and the new applications which are being developed in these artificially engineered materials at the atomic level. Although a number of systems have been grown as structurally high quality superlattices the determining factors for superlattice growth with sharp interfaces are not easy to ascertain. It is commonly accepted that in order to grow high quality superlattices, lattice matching is a necessary and sufficient condition. The sharpness of the interface is expected to be controlled by the kinetics and it is hoped that for low enough substrate temperatures, superlattices with atomically flat interfaces can be grown. We show here that the thermodynamic phase diagram of the constituents also plays a role and it might be the limiting factor in the sharpness of the interface in some cases, particularly in metallic superlattices.

The growth of single crystal epitaxial films has been the subject of intensive studies for many years.⁴ A large number of single crystal epitaxial films have been grown⁵ although a detailed, predictive understanding is perhaps only recently emerging. It is, however, quite extensively documented⁵ that high quality

epitaxial films can be grown even if lattice matching is absent.

Superlattices have been the subject of intense studies in recent years,^{1-3,6} and it is commonly accepted that lattice matching is a *sine qua non* condition for proper superlattice growth.¹ The main structural characteristic that defines a superlattice is the appearance of high angle superlattice diffraction peaks indicating that a coherent atomic stacking is present along the growth direction.^{7,8} If the constituents are lattice matched sharp superlattice peaks, narrow rocking curves and single crystal in-plane structure is observed for carefully prepared samples. Archetypal examples of these type are the semiconducting GaAs/AlAs and metallic Cu/Ni superlattices. The determination of the interface width however requires detailed modeling^{7,8} including the use of parameters such as scattering factors, Debye-Waller coefficients, polarization factors, etc. which might be strongly modified in very thin films. In general, it seems that semiconducting superlattices exhibit sharper interfaces than metallic ones.

As a rule, combination of elements that are lattice matched also exhibit solid solutions in their thermodynamic phase diagram.⁹ Possibly both facts are linked, and several ideas have been advanced on the possible relationship of

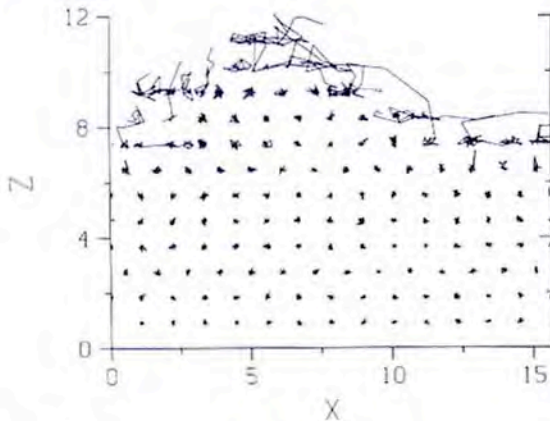


Fig. 1. Trajectory plot for the Lennard-Jones ("metal") potential showing the high mobility at the growing front. Notice the intermixing and exchange of particles approximately 3-4 atomic planes from the surface.

crystal structure and thermodynamic phase diagram.¹⁰ The relationship between epitaxy and thermodynamic phase diagrams is not yet understood. Generally, kinetic arguments are invoked for the understanding of epitaxy with little attention being paid to thermodynamics. These facts led me to explore the possible connection between superlattice growth and thermodynamic phase diagram in systems that form solid solution and are lattice matched.

In a series of extensive numerical simulation studies¹¹⁻¹³ using molecular dynamics we have tried to understand the determining factors in epitaxial growth. In the molecular dynamics calculations a temperature controlled substrate is constructed in the computer and particles, with well defined energy distribution (to simulate MBE, sputtering, etc.), are made to impinge on it. Once the interatomic potential is given, the full classical equation of motion of all the particles are calculated without any further assumptions. In general, metals are simulated using spherically symmetric potentials, such as the Lennard-Jones potential, whereas semiconductors require more complicated potentials which include three body interactions, such as the Stillinger-Weber¹⁴ potential used for silicon.

In relation to the problem at hand, it is interesting to study the trajectory of particles during the epitaxial growth. Figure 1 shows trajectory paths of Lennard-Jones particles ("metals") at typical epitaxial temperatures

followed for 200 psec.¹¹ Close to the substrate the particles execute limited motions around their equilibrium position however the surface is considerably more mobile. A high degree of mobility, and exchange of particles are observed 3-4 atomic planes from the surface. Because of this, particles move from lattice sites having high coordination (below the surface) to sites with lower coordination on the surface. The implication is that for spherically symmetric potentials considerable intermixing will occur 3-4 atomic layers from the interface. This can be understood intuitively since "spheres" can slide around each other with relative ease thus having a higher mobility and thereby "healing" defects in an effective fashion. The considerable intermixing which occurs 3-4 monolayers from the growth front suggests that at typical epitaxial temperatures thermodynamics might be important for epitaxy. The situation with the four fold coordinated Stillinger-Weber potential¹⁴ ("silicon") is however different, as shown in a similar plot in Fig. 2. The exchange of particles at the growing front is much less in this case, because the bond bending forces allow less mobility. The implication is therefore, that semiconductor interfaces could perhaps be sharper than metallic ones since the intermixing is probably less. I would like to stress at this point that these numerical calculations should be taken as suggestive of the physical phenomena operational and should not be applied in detail to real systems such as a specific element or compound.

A comparison of the experimentally determined epitaxial temperatures needed for optimum superlattice growth and temperatures extracted from the phase diagram are revealing in this context (Fig. 3). In systems that form solid solutions in their thermodynamic phase diagram the phase lines separating the liquid from the solid in the alloy is generally the weighted mean of the melting temperatures of the constituents. We designate as the "phase diagram temperature" the mean value of the two melting temperatures and its error the two extrema. A plot of the epitaxial versus the phase diagram temperature (Fig. 3), although it has large error bars, shows a clear cut correlation between these two quantities. If only kinetics were important for superlattice growth, a correlation is not expected between a kinetic and a purely thermodynamic quantity. This, together with the molecular dynamics simulation, which shows considerable intermixing, is strong indication that thermodynamics plays an important role and it is perhaps the limiting factor for the sharpness of interfaces in metallic systems that form solid solutions.

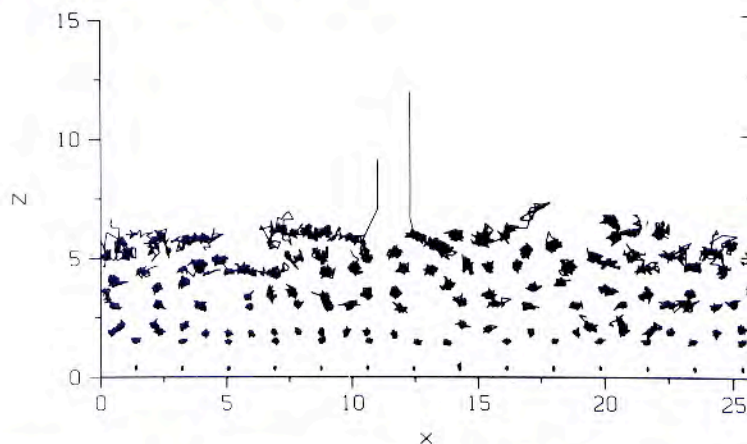


Fig. 2. Trajectory plot for the Stillinger-Weber ("silicon") potential showing

the low mobility of this four-fold coordinated potential.

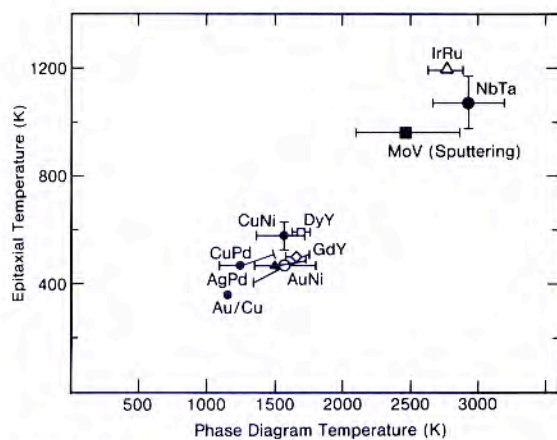


Fig. 3. Epitaxial temperature versus phase diagram temperature showing that for superlattice growth a correlation exists between the growth temperature and a purely thermodynamic quantity. The error bars in the epitaxial temperature are the limits for proper growth claimed in the literature and the error bars in the phase diagram are given by the melting points of the superlattice constituents:
 Nb/Ta,^{15,16} Pd/Ag,¹⁷ Cu/Ni,^{18,19} Ru/Ir,²⁰ Gd/Y,²¹ Dy/Y,²² Au/Ni,²³ Cu/Pd,²⁴ Mo/V.²⁵

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References

1. See various articles in "Synthetic Modulated Structures", L.L. Chang and B.C. Giessen, Academic Press Inc., Orlando (1985).
2. See various articles in "Interfaces, Superlattices, and Thin Films", J.D. Dow and I.K. Schuller, Materials Research Society Publishers, Pittsburgh (1987).
3. I.K. Schuller and H. Homma, MRS Bulletin XII, 18 (1987).
4. J.D. Matthews, "Epitaxial Growth", Academic Press, New York (1975).
5. E. Grunbaum, in "Epitaxial Growth", J.D. Matthews ed., Academic Press, New York (1975).
6. I.K. Schuller, Chapter in "Physics, Fabrication and Application of Multilayered Structures", P. Dhez and C. Weisbuch, editors (in press).
7. See for instance, D.B. McWhan, in ref. 1, p. 43.
8. I.K. Schuller, Phys. Rev. Lett. 44, 1597 (1980).
9. See for instance, K.P. Staudhammer and L.E. Murr, "Atlas of Binary Alloys - A Periodic Index", Marcell Dekker, Inc., New York (1973).

10. See for instance, T. B. Massalski, Chapter 4 in "Physical Metallurgy", R. W. Cahn and P. Haasen eds., North-Holland Publishing, Amsterdam, (1983).
11. M. Schneider, A. Rahman, and I.K. Schuller, *Phys. Rev. Letters* 55, 604 (1985).
12. M. Schneider, A. Rahman, and I.K. Schuller, *Phys. Rev.* B34, 1802 (1986).
13. M. Schneider, I.K. Schuller, and A. Rahman, *Phys. Rev.* B36, 1340 (1987).
14. F.H. Stillinger and T.A. Weber, *Phys. Rev.* B31, 5262 (1985).
15. S.M. Durbin, J.E. Cunningham, M.E. Mochel, and C.P. Flynn, *J. Phys. F: Met. Phys.* 11, L223 (1981).
16. S.M. Durbin, J.E. Cunningham, and C.P. Flynn, *J. Phys. F: Met. Phys.* 12, L75 (1982).
17. G.E. Henein and J.E. Hilliard, *J. Appl. Phys.* 55, 2895 (1984).
18. T. Tsakalakos and J.E. Hilliard, *J. Appl. Phys.* 55, 2885 (1984).
19. E.M. Gyorgy, J.F. Dillon, D.B. McWhan, L.W. Rupp Jr., and L.R. Testardi, *Phys. Rev. Lett.* 45, 57 (1980).
20. J.E. Cunningham and C.P. Flynn, *J. Phys. F: Met. Phys.* 15, L221 (1985).
21. J. Kwo, E.M. Gyorgy, D.B. McWhan, M. Hong, F.J. DiSalvo, C. Vettier, and J.E. Bower, *Phys. Rev. Lett.* 55, 1402 (1985).
22. M.B. Salamon, S. Sinha, J.J. Rhyne, J.E. Cunningham, R.W. Erwin, J. Borchers, and C.P. Flynn, *Phys. Rev. Lett.* 56, 259 (1986).
23. W.M.C. Yang, T. Tsakalakos, and J.E. Hilliard, *J. Appl. Phys.* 48, 876 (1977).
24. M.G. Karkut, D. Ariosa, J.-M. Triscone, and Ø. Fischer, *Phys. Rev.* B32, 4800 (1985) and *Physica* B135, 182 (1985).