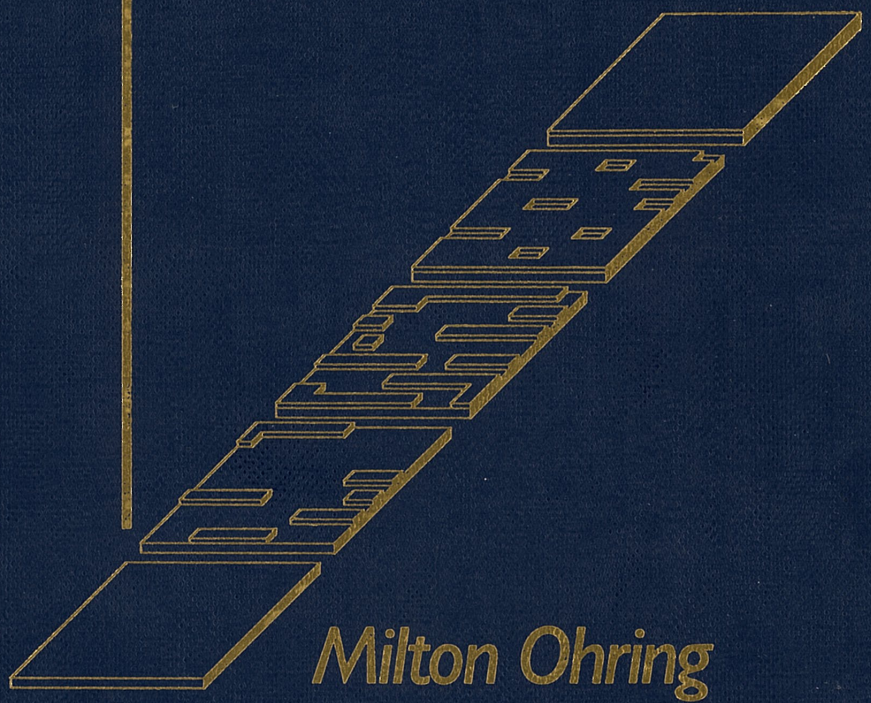
The MATERIALS SCIENCE of THIN FILMS



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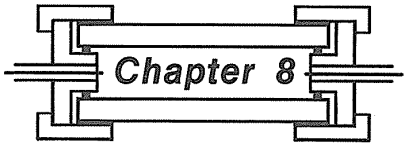

Interdiffusion and Reactions in Thin Films

8.1. Introduction

There is hardly an area related to thin-film formation, properties, and performance that is uninfluenced by mass-transport phenomena. This is especially true of microelectronic applications, where very small lateral as well as depth dimensions of device features and film structures are involved. When these characteristic dimensions (d) become comparable in magnitude to atomic diffusion lengths, then compositional changes can be expected. New phases such as precipitates or layered compounds may form from ensuing reactions, altering the initial film integrity. This, in turn, frequently leads to instabilities in the functioning of components and devices that are manifested by such effects as decrease in conductivity as well as short- or even open-circuiting of conductors, lack of adhesion, and generation of stress. The time it takes for such effects to evolve can be roughly gauged by noting that the diffusion length is given by $\sim 2\sqrt{Dt}$, where D and t are the appropriate diffusivity and time, respectively. Therefore $t \approx d^2/4D$. As we shall see, D values in films are relatively high even at low temperatures, so small film dimensions serve to make these characteristic times uncomfortably short. Such problems frequently surface when neighboring combinations of materials are chemically reactive.

For example, consider the the pitfalls involved in designing a Cu–Ni film couple as part of the contact structure for solar cells (Ref. 1). Readily available high-temperature data in *bulk* metals extrapolated to 300 °C yield a value of 3.8×10^{-24} cm^2/sec for the diffusion coefficient of Cu in Ni. For a 1000Å thick Ni film, the interdiffusion time is thus predicted to be $(10^{-5})^2/4(3.8 \times 10^{-24})$ sec, or over 200,000 years! Experiment, however, revealed that these metals intermixed in less than an hour. When colored metal films are involved, as they are here, the eye can frequently detect the evidence of interdiffusion through color or reflectivity changes. The high density of defects, e.g., grain boundaries and vacancies, causes deposited films to behave differently from bulk metals, and it is a purpose of this chapter to quantitatively define the distinctions. Indeed, a far more realistic estimate of the Cu–Ni reaction time can be made by utilizing the simple concepts developed in Section 8.2. Other examples will be cited involving interdiffusion effects between and among various metal film layer combinations employed in Si chip packaging applications. Practical problems associated with making both stable contacts to semiconductor surfaces and reliable interconnections between devices have been responsible for generating the bulk of the mass-transport-related concerns and studies in thin films. For this reason, issues related to these extremely important subjects will be discussed at length.

While interdiffusion phenomena are driven by chemical concentration gradients, other mass-transport effects take place even in homogeneous films. These rely on other driving forces such as electric fields, thermal gradients, and stress fields, which give rise to respective electromigration, thermomigration, and creep effects that can similarly threaten film integrity. The Nernst–Einstein equation provides an estimate of the characteristic times required for such transport effects to occur. Consider a narrow film stripe that is as wide as it is thick. If it can be assumed that the volume of film affected is $\sim d^3$ and the mass flows through a cross-sectional area d^2, then the appropriate velocity is d/t. By utilizing Eq. 1-35, we conclude that $t \approx RTd/DF$. Large driving forces (F), which sometimes exist in films, can conspire with both small d and high D values to reduce the time to an undesirably short period. As circuit dimensions continue to shrink in the drive toward higher packing densities and faster operating speeds, diffusion lengths will decrease and the surface-area-to-volume ratio will increase. Despite these tendencies, processing temperatures and heat generated during operation are not being proportionately reduced. Therefore, interdiffusion problems are projected to persist and even worsen in the future.

In addition to what may be termed reliability concerns, there are beneficial mass-transport effects that are relied on during processing heat treatments in

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