TREATISE ON MATERIALS SCIENCE AND TECHNOLOGY

VOLUME 24

PREPARATION AND PROPERTIES OF THIN FILMS

Edited by

K. N. Tu

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VOLUME 24

Preparation and Properties of Thin Films

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Preface

The thin film is a form of material that finds applications in many modern electronic, magnetic, optical, and energy-related devices. In these applications a detailed understanding of thin-film properties and their dependence on structure, composition, and patterning is indispensable. This volume emphasizes the progress made in the preparation of thin films and the corresponding study of their properties. Full control of film preparation, combined with modern physical analyses, is essential in advancing our knowledge about submicron structures in VLSI electronics and about near-surface phenomena and interfacial properties. We believe that the time has come to introduce these topics to scientists and engineers who are interested in thin films.

We are grateful to Professor Herbert Herman of the State University of New York at Stony Brook and the staff of Academic Press for encouraging us to compile this work, to the contributors for their effort in this serious undertaking, to the management at IBM for support, and to Lorraine Miro and Wessie Wilson for secretarial work.

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Introduction

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Preparation and Property Correlations in Thin Films

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In order to pursue a systematic thin-film study in the coming era of very large-scale integration (VLSI), where a premium is paid for generation of processes for miniaturization of microelectronic devices, there are in general four critical problem areas to consider. The first is thin-film preparation, the second is thin-film patterning (the fabrication of small structures of micron and submicron dimensions), the third is thin-film characterization (both structure and composition), and the fourth is thin-film properties (their correlation with structure, composition, and pattern). The theme of this volume is to illustrate some of the unique structure–composition–pattern–property correlations.

The capability of controlling thin-film microstructure, composition, and dimension is of increasing importance in thin-film applications. As microelectronics devices are made with denser and denser integration of circuits, the demand for unique and reliable properties of thin films has increased dramatically and many recent improvements have been achieved in the control of microstructure and composition. Consider as an example the case of metallic silicide contacts to Si. We can prepare epitaxial single-crystal, textured, polycrystalline, or amorphous silicide contacts. Then, by using ion implantation, we can introduce various dopants and impurities near the contact interface to influence contact properties such as Schottky barrier height and contact resistance. As the contact area decreases and becomes more shallow, the contact resistance rises rapidly and quickly becomes a limitation on the device performance. In addition to the technological relevance of submicron structures, there are basic scientific studies which are now in the beginning stages using these structures; for example, the use of thin-film weak links in superconductivity studies and the use of long and narrow thin-film lines in conduction localization studies. Hence, it is unique to thin-film research that one can not only correlate structure and composition with properties, but also various patterns with properties.

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To understand and utilize the correlation between the different phases of thin-film study we must learn the necessary techniques to control thin-film structure and composition and to make the submicron patterns required for specific studies. This volume, following this introductory chapter (Part I), is therefore organized into three parts. In Part II, we emphasize the variation of microstructure of thin films and the study of physical properties of these films. By many techniques we can prepare epitaxial single-crystal thin films or multilayers—a stack of thin films—to form man-made superlattices. Bicrystal, textured, randomly oriented polycrystalline, fine-grained, and amorphous thin films can also be prepared in a controlled manner. Stresses in films and structure-related stress relaxation become important contributions to instability in various device structures such as Josephson tunnel junctions and are treated in detail. In Part III, the emphasis is placed on variation of the composition of thin films and related studies. Because the film thickness is of the order of the ion penetration depth for typical implantation studies, the composition of a thin film can be tailored by ion beam techniques; for example, a small compositional change can be achieved using ion implantation and at the same time a substantial change can be brought about by ion beam mixing. Then, a continuous compositional change can be obtained by codeposition using two *e*-guns whereas a fixed composition of an alloy or compound can be produced by sputtering techniques. A thorough summary of the state of understanding of shallow silicide formation and diffusion barrier effects is included as an example of the complex metallurgical situations that are evolving under the more stringent process requirements of miniaturization. In Part IV, a novel approach to submicron patterning is illustrated as one means of achieving ultrasmall structures and of investigating and utilizing the physical properties associated with such structures.

As we witness increasingly more rapid progress in thin-film studies and applications, it becomes more difficult to prepare a book that will cover the subject completely. For this reason, certain areas have been omitted in this volume, such as the preparation and properties of amorphous thin films and large-area thin films in storage and solar energy applications. Nevertheless, we hope that these and other omissions will have a negligible effect on this volume's modest goal of showing the potential use of thin films in basic and applied studies. In the following, a brief introduction to subsequent chapters is given.

Molecular Beam Epitaxy of Superlattices in Thin Films (Chapter 2)

Interest in the Group III–V semiconductor family has derived largely from the ability to separately manipulate energy band gap and lattice spacing by composition control. This has allowed the fabrication of a multitude of devices utilizing heterojunctions for the control of electron transport, e.g., the double-heterojunction (DH) laser, high-efficiency solar cells, GaAs bipolar transistors, superlattices, and modulation-doped GaAs MESFETs. The author, Gossard, in concentrating on the latter two, illustrates important characteristics of the epitaxial growth process and electron behavior at the heterojunction.

Molecular beam epitaxy (MBE) has become a useful experimental tool for deposition of high-quality pure films and the fabricated superlattice structures described in Chapter 2 were prepared by that technique. The control made possible by MBE was illustrated by the author, who deposited distinguishable layers about 10 Å thick of alternating GaAs and AlGaAs films. A wealth of detail about crystal growth processes may be achieved in studying ultrathin layers. Also, x-ray techniques employed with the superlattice clearly showed compositional variations produced during growth and anneal. Many different ordered superlattice structures are illustrated.

Although the original intent behind fabricating the superlattice was to observe novel electron transport perpendicular to the layers, one of its most interesting applications is the use of the in-plane transport characteristics. In the "modulation-doped" structure, AlGaAs layers are *n*-doped and intervening GaAs layers are left intrinsic. Because of the difference in conduction-band-edge energy, electrons spill into the GaAs near the interface and these electrons are able to move freely in it since the donor scattering centers are in the AlGaAs. Mobilities as high as 10^5 cm/s have been observed at liquid nitrogen temperatures. Applications of superlattice structures of this type to electronic devices are now being pursued in many laboratories.

The author also points out that because of the relatively thin layers, defects such as misfit dislocations may not form. In addition to improving present devices, such as superlattice lasers instead of the more degradable DH lasers, this could also open opportunities for the use of heterojunctions between materials heretofore considered incompatible because of nonideal lattice matching.

Epitaxial Growth of Silicon Structures—Thermal, Laser-, and Electron-Beam-Induced (Chapter 3)

In Chapter 3, Lau and Mayer explore the details by which amorphous films are transformed into polycrystalline or epitaxial layers by either solid-state thermal or beam annealing techniques. As a consequence of more complex device processing and the need to produce high-quality semiconductor layers at subnormal epitaxy temperatures, this subject has been receiving increased attention in recent years. Unfortunately, because a fundamental understanding of the mechanisms by which films transform has been elusive, a persistent opinion has it that high-quality films cannot be achieved by deposition and regrowth.

Lau and Mayer observe that the differences between deposited and ion-implanted and regrown amorphous silicon are mainly associated with interface contamination and impure films. In the implanted films where no contamination is present, epitaxial layer growth is impeded only if the amorphous layer is doped. With oxygen at the interface of a deposited layer and the substrate, initiation of the epitaxial growth process requires an initial time delay. This becomes important when the time delay is of the order of the incubation time for critical polycrystalline nucleation and growth, as measured by the authors, and the two processes, epitaxy and polycrystal nucleation, become competitive. On clean substrate surfaces, the authors find that deposited films have no delay time and are equivalent in quality to implanted and annealed structures. Also, recrystallization by cw laser scanning will not help the problems caused by interface contamination, but pulsed laser anneal in the regions where the absorption depth is higher than the deposited film thickness, will result in good epitaxial films.

With the teaching of this chapter and the increased availability of high-vacuum equipment and other *in situ* surface cleaning techniques, such as ion beam bombardment, it may be possible to prepare low-temperature high-quality device structures with a wider variety of vertical structures.

Characterization of Grain Boundaries in Bicrystalline Thin Films (Chapter 4)

It has been recognized that many important characteristics of thin-film layers are related to the properties of grain boundaries and interfaces in these layers as well as the intrinsic properties of the materials involved. This is a consequence of the relatively small grain size and high density of boundaries in deposited films. Detailed structure analysis and characterization of grain boundaries are therefore important considerations for the understanding and control of desirable film properties. In Chapter 4, Cosandey and Bauer review the present state of understanding of the detailed atomic configurations in various boundary types, properties associated with boundaries, methods of preparation of desired boundaries, and characterization techniques. Extension of the concepts to layer interfaces and boundaries between dissimilar materials appears to be readily achievable and would be of importance for many practical applications in device environments such as contact reactions, electromigration, and diffusion barriers.

This chapter considers a wide range of boundaries from low-angle to high-angle and specially oriented structures. Geometric and energetic models are reviewed, illustrating dislocation models for low-angle boundaries extending to complex coincidence site configurations involving atomic and rigid-body relaxations. Properties related to the character of the boundaries described are classified as chemical, e.g., solute segregation and second phase formation; kinetic, e.g., nonequilibrium processes such as diffusion; and electrical, e.g., grain boundary scattering of electrons or electromigration.

Fabrication of known boundaries is necessary to begin to develop the type of fundamental information that will move thin-film technology and metallurgical interactions into a more fundamental mode of investigation. To accomplish this, the authors have developed an epitaxial technique in which they deposit metal films onto bicrystal substrates. Detailed study by high-resolution TEM and lattice fringe imaging has resulted in a more systematic verification of the atomistic models than we had before and provides assurance that detailed structure–property relationships are at hand.

Mechanical Properties of Thin Films on Substrates (Chapter 5)

Many degradation modes in electronic devices in which thin films are an integral part are caused by the inability of films to withstand the high stresses resulting from device fabrication procedures. Chapter 5 deals mainly with stress induced by differences in the thermal expansion coefficients of film and substrate, e.g., in soft films like lead, where residual growth stress is low. The authors, Murakami, Kuan, and Blech, attempt to provide detailed descriptions of a biaxial strain model, strain relaxation mechanisms to relieve the stress, and application to understanding the role of grain structure and surface condition in lead alloy films used in Josephson junction devices.

A deformation map is presented in which the dominant strain relaxation mechanism is calculated as a function of stress and temperature. From the map, it was determined that dislocation glide is most important at high stress and at temperatures below room temperature, which would apply, for example, in the Josephson junction case, for cooling to operating temperature (liquid He). On annealing at or above room temperature, diffusional creep is controlling. For the latter case, grain boundary diffusion