

A micrograph showing a crystallization front. A bright, irregular, and somewhat elongated region, colored in shades of yellow, orange, and red, is set against a dark blue background. The boundary between the bright region and the dark background is jagged and irregular, suggesting a complex growth process. The overall image has a grainy, high-magnification appearance typical of microscopy.

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Eric J. Mittemeijer

Metal-Induced Crystallization

Fundamentals and Applications



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PAN STANFORD  PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Metal-Induced Crystallization: Fundamentals and Applications

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ISBN 978-981-4463-40-9 (Hardcover)

ISBN 978-981-4463-41-6 (eBook)

Printed in the USA



Metal-Induced Crystallization

Preface

Crystalline semiconductors, often in the form of thin films, are crucial materials for many modern, advanced technologies in fields such as microelectronics, optoelectronics, display technology, and photovoltaic technology. Unfortunately, thin films of semiconductors produced by vapor deposition techniques are usually in a low-performance, amorphous form. The transformation of low-performance, amorphous semiconductors into high-performance, crystalline semiconductors is one of the most important and most challenging steps to advance the above-indicated technologies.

Metals in contact with amorphous semiconductors can induce the crystallization of these amorphous semiconductors at surprisingly low temperatures (as low as 120°C). This so-called metal-induced crystallization (MIC) process was firstly observed more than 40 years ago. In recent years, the MIC process has attracted great scientific and technological interest because it principally allows the production of crystalline semiconductor-based advanced devices at low temperatures directly on heat-sensitive components, such as plastics, which would otherwise have not been possible.

As a result of numerous investigations by different research groups all over the world, the fundamental aspects of the MIC process in various metal/amorphous semiconductor systems have now been disclosed, partly in great detail. MIC represents an intriguing solid-solid phase transformation phenomenon occurring/initiating particularly at surfaces and interfaces in thin-film (nano)systems. In such systems, the phase transformation is not simply controlled by bulk thermodynamics: the (excess) Gibbs energy associated with surfaces and interfaces in the systems may play a significant or even dominant role. Moreover, the kinetics of phase transformation in thin-film (nano)systems can be quite different from that in bulk systems, for example, because of the presence of a relatively large amount of defects (as grain boundaries and dislocations), possibly also providing fast diffusion paths. Fundamental research on the MIC process thus presents an attractive road to deeper insight into the role of interface energetics and kinetics in solid-solid phase transformations.

Advances in the fundamental understanding of the MIC process have resulted in pronounced progress in sophisticated applications of the MIC process in many technologies. This, for example, holds for the production of high-efficiency, low-cost, thin-film crystalline silicon solar cells of advanced flat-panel displays, and of Blu-ray data storage devices.

The present book, for the first time, summarizes the existing knowledge and broad range of applications of the MIC process of amorphous semiconductors. The book firstly addresses the current knowledge and achieved fundamental understanding of MIC processes (Chapters 1–4). Next, the book elucidates how to employ MIC processes in advanced technologies, for example, in novel, state-of-the-art solar cell and display technologies (Chapters 5–7). The aim is to give the reader a comprehensive perspective of the MIC process and thereby to stimulate the future development of novel crystalline semiconductor-based thin-film technologies.

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Winter 2014

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Chapter 1

Introduction to Metal-Induced Crystallization

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This chapter gives a historical overview of research performed on the metal-induced crystallization (MIC) process. The MIC temperatures and behaviors for a wide range of metal/amorphous semiconductor systems, as reported in the literature (data obtained using different experimental approaches), have been summarized and tabulated. The development of an understanding of the mechanisms controlling MIC, and related phenomena such as layer exchange, as well as the technological applications of these processes have been sketched as an introduction to later chapters of this book.

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Metal-Induced Crystallization: Fundamentals and Applications

Edited by Zumin Wang, Lars P. H. Jeurgens, and Eric J. Mittemeijer

Copyright © 2015 Pan Stanford Publishing Pte. Ltd.

ISBN 978-981-4463-40-9 (Hardcover), 978-981-4463-41-6 (eBook)

www.panstanford.com

1.1 A Brief History of Metal-Induced Crystallization

In 1969, Oki et al. [1] observed that amorphous Ge (a-Ge) crystallizes at surprisingly low temperatures when it is in contact with a metal such as Al, Ag, Au, Cu, or Sn. Shortly thereafter, Bosnell and Voisey reported that such decreased crystallization temperatures also occur for amorphous Si (a-Si) in contact with a metal [2]. In both studies, the amorphous semiconductors (and the metals) were prepared by vacuum evaporation and an electron diffraction technique was used to detect the occurrence of crystallization. Thereafter, more detailed electron microscopic investigations of this striking effect were carried out by Herd et al. [3] and Ottaviani et al. [4–6], and this phenomenon was named *metal-contact-induced crystallization* [3], nowadays usually referred to as *metal-induced crystallization* (MIC).

The MIC process was found to be associated with intermixing of the semiconductor and the metal, and small crystallites of Si or Ge could indeed be found to have formed in the metal [3–6]. On the basis of these observations, the MIC effect was interpreted as the result of initial dissolution of the semiconductor into the metal, followed by precipitation of the crystalline semiconductor out of the metal matrix [4–6]. An important role of fast atomic transport along the metal/semiconductor interface was indicated in these early studies [3–6]. A very different interpretation of the MIC effect was given by Brodsky and Turnbull [7], who instead suggested that MIC would be mediated by the formation of a low-temperature eutectic melt caused by lowering of the binary eutectic temperature when one of the two components (i.e., the semiconductor) is amorphous.

As compared to the above-described early interpretative efforts, understanding of the MIC process was greatly advanced in the early 1990s by the application of in situ heating transmission electron microscopy (TEM) techniques, which were developed in the late 1980s. By employing in situ heating high-resolution transmission electron microscopy (HRTEM), the MIC process in layered structures of simple eutectic metal semiconductor systems, such as crystalline Al (c-Al)/a-Si [8], crystalline Ag (c-Ag)/a-Ge [9], and c-Ag/a-Si [10], was investigated. It was shown that the MIC process does not involve the formation of any liquid phase: it is a fully solid-state

process [8–12]. Furthermore, no formation of any (metastable) metal semiconductor compound(s) was detected during MIC in such systems [8–12]. The MIC process in a compound (silicide)-forming system such as Ni/a-Si was also investigated by in situ heating HRTEM [13, 14]. It was concluded in this work that in such a system MIC is mediated by the initial formation of a solid silicide phase (NiSi_2), which subsequently migrates into/within the a-Si film with formation of a crystalline Si (c-Si) phase in the wake of the NiSi_2 [13, 14].

In the late 1990s, (related) processes such as metal-induced layer exchange (MILE) [15–17] and metal-induced lateral crystallization (MILC) [18–20] were identified. It was found that upon MIC in, for example, a c-Al/a-Si bilayer, the Al and Si sublayers exchange their original locations [15]. As a result, a nearly continuous c-Si layer is formed at the original location of the metal (Al) sublayer at low temperatures (see Fig. 1.1D). Such a MILE process can be very useful for low-temperature production of thin-film crystalline semiconductors, in particular for thin-film photovoltaic applications (see Chapter 5). In MILC, a compound (e.g., silicide)-forming metal (e.g., Ni or Pd) is firstly grown in a patterned way on top of an amorphous semiconductor layer (e.g., a-Si). Upon annealing, it was found that the crystalline modification of the semiconductor not only grew at the metal-covered region but also grew laterally outside the metal coverage (see, e.g., Fig. 1.2D,E). Such MILC can be very useful for low-temperature preparation of polycrystalline Si thin films for applications in thin-film transistors in advanced flat-panel displays (see Chapter 6).

The thermodynamics and kinetics of MIC and MILE processes have been investigated systemically since 2003 in our research group led by Prof. Mittemeijer [21–37]. A unified, quantitative understanding of the MIC process occurring in various metal-semiconductor systems has been achieved on the basis of *interface thermodynamics*. On this basis the very different MIC temperatures and behaviors in a wide range of metal/amorphous semiconductor systems have been successfully predicted [29, 30, 33] (see Chapter 2). The *kinetics* of MIC and MILE were described on the basis of quantitative evaluation of the (inter)diffusion kinetics in metal/semiconductor layered systems by using Auger electron spectroscopy (AES) depth profile measurements [21, 23, 28] (see Chapter 3). Very recently, advanced

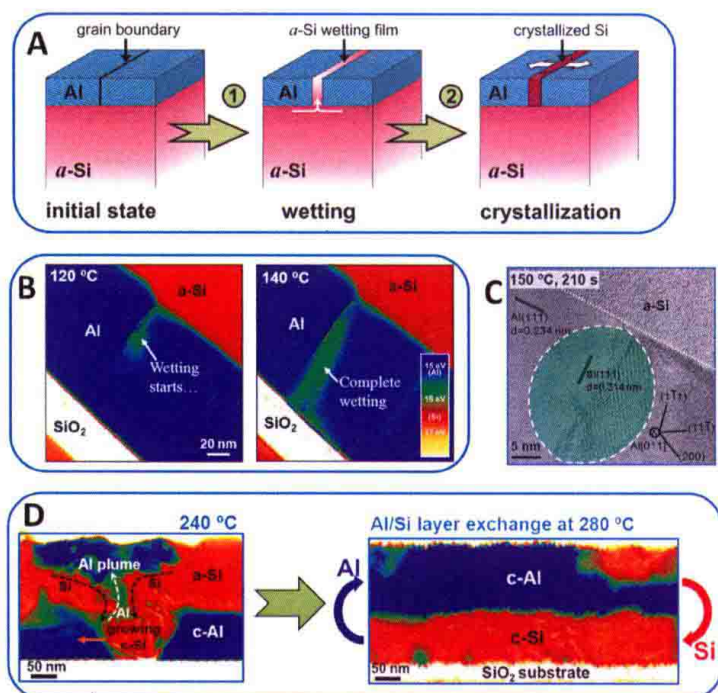


Figure 1.1 (A) Schematic illustration of the mechanism of Al-induced crystallization of a-Si in c-Al/a-Si bilayers. Initially, GBs in the Al overlayer get "wetted" by a-Si. Beyond a critical thickness of the "wetting" a-Si film at a temperature above 140 °C, crystallization initiates at these "wetted" Al GBs and the formed c-Si grain subsequently grows laterally in the Al overlayer. Reprinted with permission from Ref. [33], Copyright 2009, John Wiley and Sons. (B) In situ heating valence energy-filtered TEM observation of "wetting" of an Al GB by a-Si during annealing of a 100 nm c-Al/150 nm a-Si bilayer. The increase in the plasmon loss energy at the location of the Al GB near the c-Al/a-Si interface observed at 120 °C (left) demonstrates the initial "wetting" of the Al GB by Si. Complete "wetting" of the Al GB by Si has been realized at 140 °C (right). Reprinted with permission from Ref. [36], Copyright 2011, John Wiley and Sons. (C) In situ heating HRTEM observation (cross-sectional view) of the nucleation of c-Si at a high-angle Al GB at 150 °C. Reprinted with permission from Ref. [36], Copyright 2011, John Wiley and Sons. (D) In situ valence energy-filtered TEM observation (cross-sectional view) of a 150 nm a-Si/100 nm c-Al bilayer upon heating at 240 °C, showing the growth of a c-Si nucleus in the Al bottom layer and, at the same time, the development of a mushroom-shaped Al "plume" of cloud-like morphology in the a-Si top layer. Upon heating at 280 °C, Si and Al sublayers have practically exchanged their locations: layer exchange has occurred. Reprinted with permission from Ref. [37], Copyright 2012, American Chemical Society. *Abbreviation:* GB, grain boundary.

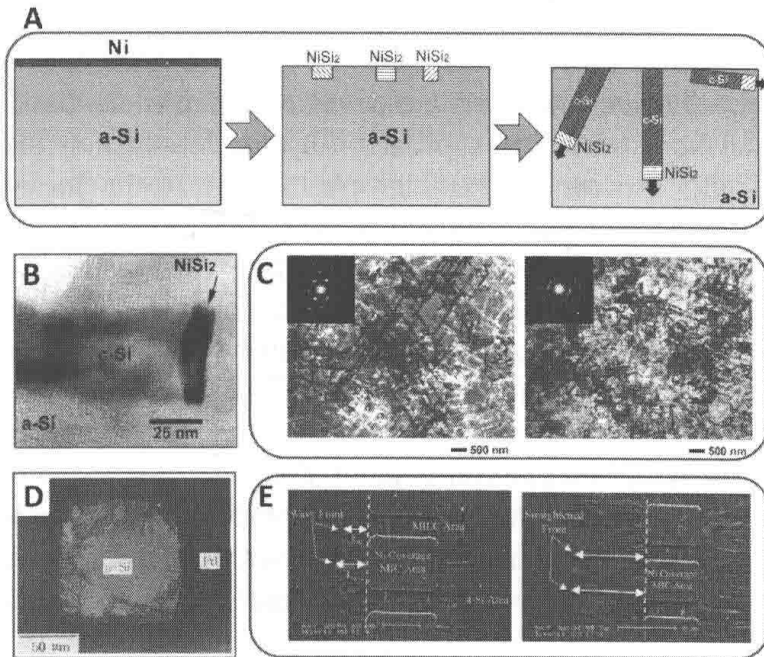


Figure 1.2 (A) Schematic illustration of the mechanism of Ni-induced crystallization of a-Si in c-Ni/a-Si bilayers. Upon heating, initially Ni reacts with a-Si to form NiSi₂ at the c-Ni/a-Si interface. c-Si then nucleates at the interface between NiSi₂ and a-Si. Continued crystallization of c-Si is realized by migration of NiSi₂ into/within the a-Si film, leaving c-Si in its wake. (B) TEM bright-field image of a migrating NiSi₂ precipitate with grown needle-like c-Si in its wake. Reprinted with permission from Ref. [59], Copyright 2001, Elsevier. (C) TEM images of a Ni-induced crystallized a-Si film at 400°C for 10 minutes (left) and 30 minutes (right). Continued crystallization of a-Si has occurred by the repeated NiSi₂-induced growth of needle-like Si crystallites in the initial a-Si film. Reprinted with permission from Ref. [59], Copyright 2001, Elsevier. (D) Pd (4 nm layer thickness)-induced lateral crystallization of a-Si film (150 nm layer thickness) upon annealing at 500°C for 5 hours (optical micrograph). Reprinted with permission from Ref. [18], Copyright 1995, AIP Publishing LLC. (E) Ni (5 nm layer thickness)-induced lateral crystallization of a-Si film (100 nm layer thickness) upon annealing at 500°C for 7 hours (left) and 21 hours (right) (orientation imaging microscopy image). Reprinted with permission from Ref. [20], Copyright 1998, AIP Publishing LLC.

real-time in situ analytic TEM techniques have been applied to disclose the detailed atomic-scale mechanisms of MIC and MILE, which were neither observed nor even recognized before [36, 37].

Research has been directed to (potential) applications of MIC, in particular since 2000. For example, thin-film c-Si solar cells with an efficiency of higher than 8% have been developed on the basis of an Al-induced crystallization approach [38] (for details of application of the MIC process in thin-film photovoltaic technologies, see Chapter 5). Furthermore, advanced display devices with exceptional performance have been developed by utilizing the low-temperature MILC process of a-Si (for details of application of the MILC process in advanced flat-panel displays, see Chapter 6). Very recently, MIC has also been applied for the production of Blu-ray data storage devices. In this case, because of the low crystallization temperature in metal/a-Si (or a-Ge) bilayer systems, the metal/a-Si (a-Ge) bilayer crystallizes upon low-power (i.e., low-cost) laser irradiation and can therefore serve as an excellent type of data storage medium (for details of application of the MIC process in Blu-ray data storage devices, see Chapter 7).

1.2 Experimental Methods for Investigating the Metal-Induced Crystallization Process

Many different experimental techniques have been employed to investigate the MIC process. Because of different sensitivities (to crystallization) of these techniques, the reported crystallization temperature(s) as determined by different techniques can be (even very) different for the same metal/amorphous semiconductor system (see Tables 1.1 and 1.2). The key features of major techniques used for MIC investigations are briefly summarized in the following sections.

1.2.1 X-Ray Diffraction

X-ray diffraction (XRD) is one the most powerful techniques for investigating the occurrence and kinetics of a phase transformation process, such as crystallization (see Chapter 11 in Ref. [39]). Crucial information on the (initial) nucleation and (subsequent) growth of a certain crystalline semiconductor phase can be extracted from the emergence and increase of the intensities of corresponding diffraction maxima. This method can be applied both to bulk specimens and to