Editorial

Polycrystalline Silicon Thin Films for Solar Cells via Metal-Induced Layer Exchange Crystallization

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Solar photovoltaics (PV) has the potential to take center stage in global energy in the future. Today, crystalline silicon (c-Si) PV technology dominates the global PV market, with a share of about 95% [1]. C-Si solar cells are characterized by high power conversion efficiencies (PCE) of more than 20% [2]. The last decade has seen a continuous decline in the prices of PV modules, which has led to a tenfold decrease in the levelized cost of electricity [3]. To make c-Si solar cells cost-competitive in the future, significant efforts are being made to reduce the thickness of c-Si wafers, which is a significant part of the cost of the module [4]. The standard for modern c-Si PV production is wafers with a thickness of 150–200 μm. At the same time, a further reduction in the thickness to less than 100 μm is a very difficult task within the framework of modern equipment and requires revolutionary new concepts in the c-Si PV industry [5,6]. Thus, an attractive alternative approach to solar cell production is the cost-effective fabrication of high-quality crystalline Si thin films. Thin-film polycrystalline silicon (poly-Si) technology, which involves the formation of c-Si thin films with a grain size of 0.1–100 μm on low-cost large-area substrates (glass, etc.) [7], attempts to combine the economic efficiency of thin-film technology with the high quality of the crystalline material typical of c-Si technology.

It should be noted that the grain size of poly-Si films critically affects the operation of devices based on them. Increasing the grain size effectively reduces grain boundary defects and thus the recombination of charge carriers [8]. In view of this, a more suitable material for use in solar cells is films of so-called large-grain poly-Si, in which the lateral grain size is larger than the film thickness, which is typically a few micrometers [9].

The metal-induced crystallization (MIC) of amorphous silicon-containing thin films is of great scientific and technological interest and is considered as a promising method for applications such as solar cells [4,9–11] and transistors [10,11]. MIC of amorphous silicon (a-Si) is implemented in two stages. The first stage involves sequential deposition of a-Si and metal layers with thicknesses ranging from several tens to several hundreds of nanometers on a substrate in different layouts. The second stage consists of isothermal annealing of the resulting layered system [10]. MIC allows the formation of large-area large-grain poly-Si thin films at low process temperatures and, at the same time, includes the traditional furnace annealing process in an inert gas atmosphere or vacuum [11].

The low-temperature crystallization effect of thin films of amorphous semiconductors upon contact with metals (Al, Au, Ni, etc.) was discovered in the early 1970s [12]. When these metals come into contact with a-Si, a fairly local electronic interaction (covering about two Si monolayers) occurs in the interface region, resulting in the weakening of covalent bonds in a-Si [13]. This effect leads to a significant decrease (of several hundred degrees) in the crystallization temperature [14] compared to the traditional solid phase crystallization process, for which this temperature is at around 600 °C [15].

According to the nature of the interaction with silicon, the metals used in MIC are divided into two categories: metals forming compounds with Si (Ni, Pd, Pt, etc.) and those forming eutectic binary systems (Al, Au, Ag, etc.) [11]. The use of compound-forming

metals leads to metal-induced lateral crystallization, in which the movement of metal silicides through a-Si results in the formation of poly-Si [4], including in a-Si regions not originally covered with a metal film. Poly-Si obtained in this way is used to fabricate advanced thin-film transistors [11,15].

For eutectic metal/a-Si bilayer systems, the layer exchange (LE) mode of MIC of a-Si is of particular note as it is an attractive way to obtain large-area large-grain continuous poly-Si thin films for solar cell applications [4]. The LE process was first described in [16] using the Al/Si system as an example and was further demonstrated for the Ag/Si [17] and Au/Si [18] systems. The LE process is carried out at temperatures below the eutectic point; therefore, it is a solid-phase process [16]. This process leads to the replacement of the initial metal layer by a crystalline Si film during annealing of the metal/a-Si bilayer system. The LE mechanism using aluminum, aluminum-induced layer exchange (ALILE), has been studied more extensively than LE using other eutectic metals. ALILE has been studied both experimentally and theoretically [13,19–25].

The process can be divided into the following steps: (i) the weakening of covalent Si-Si bonds at the a-Si/Al interface; (ii) the transfer (diffusion) of Si atoms into the Al layer along its grain boundaries and wetting them with a-Si [22,26]; (iii) the nucleation of Si at Al grain boundaries upon reaching a thickness of approximately 4 monolayers of Si [26] (in this case, nucleation sites are different for different eutectic metals and are determined by an energy balance that accounts for the bulk Gibbs energies and changes in the surface and interface energies [13]); and (iv) the lateral growth of Si grains due to the continuous diffusion of Si atoms, their coalescence, and, ultimately, the replacement of the Al layer with poly-Si film [10]. The penetration of Al into the initial a-Si layer is due to compressive stress in the Al layer caused by the growth of Si grains in it [22]. Al penetrating into the original a-Si layer, in turn, also coalesces there to form an almost continuous Al layer [22]. Depending on the order of deposition of metal and semiconductor layers in the as-deposited sample, the conventional or inverted LE processes can be implemented. If metal and a-Si layers are arranged in the initial sample in the substrate/metal/a-Si sequence, a poly-Si film is formed directly on the substrate as a result of LE, and in this case, it is covered with an upper metal-containing layer. In the case of the inverted arrangement of layers in the initial sample (substrate/a-Si/metal), the LE process leads to the formation of a poly-Si film on a metal-containing layer [25,27,28].

The a-Si to metal thickness ratio significantly affects the morphology of the poly-Si film formed [29], whose main features are the presence of "holes" and "hillocks" [24,25,29]. In the case of conventional LE, "holes" in poly-Si are occupied by Al not involved in the LE process, and upon subsequent metal etching, they become voids (holes) in a poly-Si film [29,30]. Hillocks are crystalline silicon islands formed on the surface or under the poly-Si film (depending on the initial geometry of the layers) as a result of secondary crystallization when the metal penetrates into the initial a-Si layer [25,28]. To be used in solar cells, a poly-Si film must be continuous and at the same time have a flat surface; therefore, the presence of both holes and hillocks is undesirable [10,25]. If the thickness of a-Si is less than the thickness of Al, the poly-Si film, as a rule, is formed discontinuously and the formation of hillocks is not observed. If the thickness of a-Si is greater than that of Al, there are no holes in the poly-Si film, but hillocks grow. For example, for layers several hundred nanometers thick, an a-Si/Al thickness ratio close to 1 makes it possible to avoid the presence of holes and hillocks after the LE process [30], and an additional factor suppressing the formation of hillocks can be a decrease in annealing temperature [25].

The grain size is one of the most important structural parameters of crystalline Si thin films. The performance of semiconductor devices depends significantly on the grain size of poly-Si based on them [11,31]. Poly-Si thin films with a thickness of several hundred nanometers obtained in the LE process are often used as a seed layer for epitaxial thickening in the fabrication of solar cells. In this case, it is the seed layer that determines the grain size of the epitaxial layer [4]. The average lateral grain size in poly-Si thin films fabricated by LE varies from several hundred nanometers to several hundred micrometers [31,32].

A general approach to increasing the lateral grain size of a poly-Si film is to suppress the nucleation of Si grains during MIC [10,31]. A reduction in the nucleation density of Si is mainly achieved by lowering the annealing temperature [27,31,33], using an additional interlayer (membrane) between the metal and a-Si [31,32,34], and increasing the grain size in the metal layer [23]. Decreasing the annealing temperature slows down the Si diffusion into the metal and thus reduces the nucleation density. For example, the Si grain size obtained in ALILE increased from ~100 μm to ~400 μm [31] as the annealing temperature decreased from 450 °C to 400 °C.

An interlayer with a thickness of several nanometers created between the metal and a-Si allows one to control the flux of Si atoms into the metal film, which determines the kinetics of the LE process and the grain size of the resulting poly-Si. In conventional ALILE, AlO_x is used as an interlayer, which is usually created by exposing the deposited Al layer to the atmosphere [31,32]. Increasing the air-exposure time of the Al layer from 5 min to 24 h led to an increase in the thickness of the AlO_x formed and, consequently, to an increase in the grain size from 20 μm to 100 μm [32]. In the case of inverted ALILE, SiO_x obtained by air-exposure of an a-Si film [25] or layers obtained as a result of additional deposition [34] are used as the membrane layer.

In the LE process, the diffusion of a-Si atoms into the metal layer occurs along its grain boundaries, which has been confirmed by thermodynamic calculations [13] and also shown in in situ transmission electron microscopy studies of the process [22]. Thus, an increase in the metal grain size leads to a decrease in the flux of Si atoms into the layer, a reduction in the nucleation density of Si and hence an increase in the average poly-Si grain size [35]. It should be noted that the above approaches aimed at increasing the grain size in poly-Si, coupled with the slowing down of kinetic processes during LE, inevitably lead to an increase in the annealing time.

Along with a-Si, amorphous silicon suboxide (a-SiO_x, $0 < x < 2$) [36] is also used as the initial silicon-containing material in MIC [37,38]. The use of a-SiO_x in aluminum-induced crystallization has several advantages over the use of a-Si, such as reducing the cost of the silicon-containing thin-film precursor process by reducing vacuum quality requirements and eliminating the time-consuming air-exposure process after Al layer deposition to form the Al oxide interlayer.

For AIC of a-$SiO_{0.2}$, both conventional [39] and inverted [28] ALILE processes have been carried out. An important feature of the material obtained by ALILE using a-SiO_x is the absence of hillocks in its structure after annealing, which is important for the subsequent use of poly-Si in applications. A further increase in the oxygen content in the initial a-SiO_x led to the complete oxidation of aluminum to form the γ-Al_2O_3 phase [40]. In addition, the incorporation of Al into the SiO_2 substrate was observed, which was also accompanied by its oxidation. The formation of the γ-Al_2O_3 phase significantly complicates the chemical etching of the Al-containing layer. In contrast, in the case of gold-induced crystallization of a-SiO_x, gold does not react chemically [38] with the silicon-containing precursor, and the Au-containing layer can be removed using standard chemical etchants.

Poly-Si films fabricated by ALILE cannot by themselves be used as absorber layers in thin-film crystalline solar cells due to their high level of p-type Al doping and thicknesses of several hundred nanometers [4,11]. Thus, when creating devices, highly doped ALILE poly-Si films are used as a template for epitaxial growth of the absorber layer and also act as a back surface field in the solar cell structure [41]. Despite significant progress in this area, today the PCE of solar cells with ALILE poly-Si seed layers does not exceed 8.5% [4]. The low efficiency of the fabricated solar cells is due to the high density of intragrain defects in poly-Si layers obtained by ALILE and epitaxy [7], which means that the quality of the poly-Si material produced by MIC should be improved.

To date, there is a great deal of groundwork for the fabrication of large-grain poly-Si films on low-temperature substrates by the LE process; however, the further development of approaches aimed at reducing the density of both grain boundaries and intragrain defects is required. The possibility of controlling the main structural and morphological

characteristics of thin-film materials (grain size, continuity, smoothness of the interface) is shown, which demonstrates the great potential of the LE process using amorphous silicon-containing thin films for solar-cell applications.

Conflicts of Interest: The authors declare no conflict of interest.

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