

Growth of polycrystalline CdS and CdTe thin layers for high efficiency thin film solar cells

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Abstract

Recently, conversion efficiencies close to 16% for thin film solar cells based on the CdS/CdTe heterojunction have been reported. These relevant results, however, have not yet solved the problems which arise when industrial production is undertaken as the demand for low cost imposes constraints which considerably limit the final efficiency of the cells. In this paper, we will show that very high conversion efficiencies can still be achieved even making use of low cost soda-lime glass as substrate. In fact, the Na contained in this kind of glass diffuses during the fabrication of the cell into the active layers of the device causing a substantial decrease of the fill factor and consequently of the efficiency of the cell. In particular, we will describe the methods and the magnetron sputtering techniques used to grow a polycrystalline CdS thin film with a controlled Na content. We will also describe the details of the growth via the close-spaced sublimation (CSS) technique of the CdTe polycrystalline film, which are crucial for the heterojunction and the back contact which has been fabricated exploiting the characteristics of Sb_2Te_3 which is a low gap *p*-type semiconductor with a high conductivity. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Cadmium telluride (CdTe) is a suitable photovoltaic material for solar cells because of its optimum energy gap (1.43 eV) and high absorption coefficient for visible solar radiation. To reduce production costs, it is necessary to fabricate the solar cells with polycrystalline thin films deposited onto low-cost substrate like soda-lime glass. Because of short optical absorption length in CdTe and the difficulty of forming a thin film shallow homojunction with a high conductivity surface layer, thin film CdTe solar cells are of the heterojunction configuration. To allow the formation of the heterojunction, a transparent conducting semiconductor is used as the CdTe partner. Cadmium sulphide (CdS) has been found to be the best suited for thin film CdTe heterojunction solar cells, and conversion efficiencies of higher than 12% have been reported for CdS/CdTe solar cells prepared by several techniques. In efficient solar cells, CdS films are prepared by spray-pyrolisis, vacuum evaporation, RF sputtering and close-spaced sublimation (CSS), and CdTe films are deposited by CSS, electrodeposition, spraying, screen printing and metal-organic chemical vapour deposition (MOCVD). Each technique has its own advantages. However, the best

CdTe based thin film solar cells have been fabricated using the CSS method [1].

In this work, efficient thin film CdS/CdTe heterojunction solar cells have been prepared from CdS deposited by RF sputtering technique, and CdTe deposited by CSS, both cost-effective scalable techniques. The solar cell is of the front-wall configuration, i.e. films of CdS, *p*-type CdTe, and an ohmic contact are subsequently deposited onto a transparent conducting oxide-coated soda-lime glass (Fig. 1).

The front transparent contact has been prepared by depositing in sequence films of In_2O_3 90%: SnO_2 10% (ITO) and SnO_2 , the first one to get a low sheet resistance and the second one to passivate the soda-lime glass against Na diffusion. Besides, CdS films deposited by RF sputtering and CdTe films deposited via CSS technique on the top of the CdS layer are separately treated in a saturated cadmium chloride (CdCl_2) atmosphere at a temperature of 500 and 400°C, respectively. Following this process the CdS film is restructured, being made denser with enhanced grain size. This fact yields an improvement both in the intrinsic quality of the film (crystalline quality, grain boundaries, superficial roughness) and in its electro-optical properties. It is known that the heat treatment around 400°C with CdCl_2 has been routinely used to significantly improve electronic characteristic of polycrystalline CdS/CdTe films. Generally,

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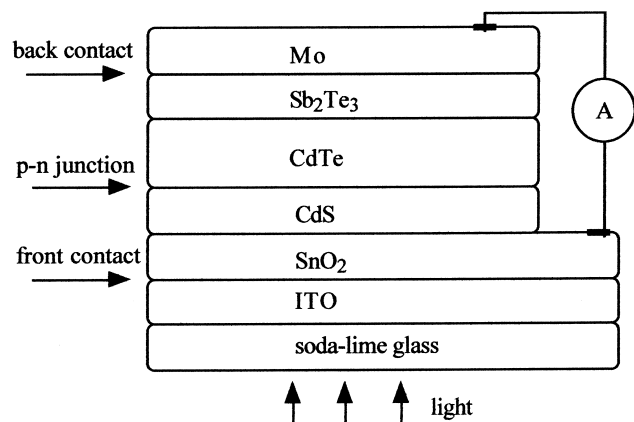


Fig. 1. CdS/CdTe thin film solar cell structure.

the CdCl_2 treatment increase the average grain size of the CdS and CdTe films, prepared with several methods such as electrochemical or vacuum deposition, which usually grow with small grain size. In the case of high temperature deposition, such as the CSS method, the as-deposited average grain size is large ($\geq 1 \mu\text{m}$) [2]. However, the CdCl_2 heat treatment is still necessary to achieve good device characteristics. There is evidence that in large grain films the treatment promotes grain boundaries re-growth and small grains elimination. In either case, CdCl_2 is believed to act as a flux agent that increases the atomic mobility of CdTe at the annealing temperature. The role of CdCl_2 is not only that of re-crystallizing the CdTe film but also to dope it *p*-type. In fact, as-deposited CdTe films have shown to be *p*-type with a resistivity of 10^4 – $10^5 \Omega \text{cm}$; this kind of conductivity is probably due to stoichiometry native defects, like Cadmium vacancies (V_{Cd}). After CdCl_2 treatment, the same films are *p*-type conductivity again but with a resistivity as low as $100 \Omega \text{cm}$. The doping of CdTe by CdCl_2 could be due to the formation of $(V_{\text{Cd}}-\text{Cl})^-$ complexes which have an activation energy of 0.05 eV, that is a shallower energy level than that of Cadmium vacancies [3]. In the more efficient cells, as back contact a Cu-graphite layer is generally used. Since Cu is a highly diffusion element into CdTe, these cells, in the long period are destined to degrade. Recently, we have developed a new back-contact which does not contain any copper or any doping element that can diffuse into CdTe. This contact is made with a thin layer of Sb_2Te_3 , which is a stable compound that exhibits a forbidden energy gap of 0.3 eV and is a degenerate *p*-type semiconductor with a resistivity of $10^{-4} \Omega \text{cm}$. The Sb_2Te_3 layer is deposited by sputtering at a substrate temperature of 300–350°C. This high substrate temperature allows the formation of a p^+ Sb_2Te_3 layer on top of CdTe film which assures, together with its low resistivity, the ohmic behaviour of the back contact. The best CdTe/CdS solar cell fabricated with these layers in our laboratory exhibits an efficiency of 14.6% that is very close to the maximum efficiency so far obtained (15.8%) [1].

2. Experimental procedure

2.1. Substrate preparation

The substrate used for the deposition is a 1 in.² soda-lime glass previously washed with a low-alkaline detergent and then carefully rinsed in deionized water. Finally, the substrate is rinsed again with acetone and propan-2-ol in an ultrasonic bath.

2.2. The transparent conducting oxide (TCO)

Due to its low cost, soda-lime glass is suitable for industrial production but this advantage is partially reduced because the sodium, contained in this type of glass, could diffuse during thermal treatments into the other layers which form the device. To avoid this problem, a passivating layer is often deposited on the soda-lime glass such as alumina (Al_2O_3) or silica (SiO_2). We are adopting a new scheme which consists in the deposition of a SnO_2 layer that allows to control the Na diffusion. The front contact is set up with $1 \mu\text{m}$ ITO (In_2O_3 90%: SnO_2 10%) and a 0.1– $1 \mu\text{m}$ SnO_2 thick films. The ITO layer is deposited via magnetron RF sputtering, under an Argon pressure of 1×10^{-2} mbar, at a substrate temperature of 450°C with a deposition rate of 5 \AA s^{-1} . The ITO film exhibits a sheet resistance of $R_s = 1 \Omega \square^{-1}$. This first deposition still allows the diffusion of sodium, from soda-lime glass, as it is evident by the appearance of NaCl crystallites when the surface of the ITO layer is treated in air at 500°C with CdCl_2 . On top of this ITO film, we deposit in sequence the SnO_2 layer with an O_2 partial pressure of 2×10^{-4} mbar keeping all the other sputtering deposition parameters constant. Under these conditions, SnO_2 grows in a very compact polycrystalline structure exhibiting a sheet resistance of $R_s = 10 \Omega \square^{-1}$. This second layer, despite its greater resistance, does not modify the overall resistance, which keeps its minimum value, with the great advantage of controlling the Na diffusion by means of the SnO_2 film thickness. Annealing these films with CdCl_2 , as previously described, we do not observe any NaCl crystallite formation if the SnO_2 layer is $1 \mu\text{m}$ thick, while there are few small NaCl crystallites if the SnO_2 film is $0.5 \mu\text{m}$ thick. These TCO films exhibit a transparency of 85% in the region of visible spectrum of interest.

2.3. The CdS layer

The good quality of a thin film solar cell is strongly dependent on the proper interaction among the different layers which constitute the device. We consequently deposited, via magnetron RF sputtering, without removing the sample from the apparatus, a 2000 Å thick layer of CdS at a substrate temperature of 200°C with a deposition rate of 5 \AA s^{-1} in an Ar pressure of 1×10^{-2} mbar. On top of the CdS film, a 1500 Å thick layer of CdCl_2 is then evaporated. Subsequently, the CdCl_2 covered CdS film is annealed in

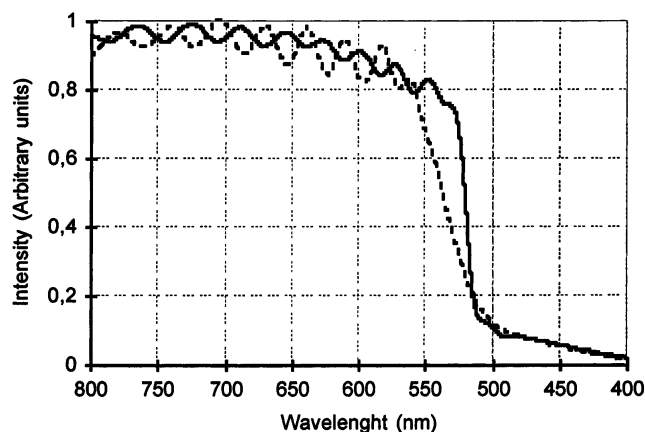


Fig. 2. Transmission spectrum of the CdS layer, before the CdCl₂ treatment (dash-dotted line) and after the treatment (solid line). The shift towards the right of the absorption edge proves the beneficial effect of the CdCl₂ treatment.

air in a two-step process, the first at 460°C and in sequence at 500°C, both steps for a duration of 20 min. The system is then washed in methanol to get rid of residual traces of CdCl₂. The first important observation that we made is that the grain size of the CdS film after treatment depends strongly on the SnO₂ film thickness. A large grain size of CdS, in the order of 2000–3000 Å, is obtained for a lower SnO₂ thickness, while, by increasing the thickness of the SnO₂ layer, the grain size of the CdS film decreases. For a SnO₂ thickness of 1 µm, the grain size of the CdS film remains as it was before CdCl₂-treatment (500 Å). We interpreted these results by taking into account the Na-diffusion from soda-lime glass; a larger grain size in the CdS film corresponds to a larger amount of Na present in the CdS film. We conclude that the Na-diffusion into the CdS film depends on the thickness of the SnO₂ layer and for a SnO₂ thickness on the order of 1 µm, the Na-diffusion is quite negligible. Anyhow, after CdCl₂ treatment, in the absence of Na, CdS films are denser and present a better crystalline quality than that of the not-treated samples [4]. This is put in evidence by observing the optical transmission spectra (Fig. 2). Besides, the X-ray diffractograms of the as-deposited CdS films show a mixture of cubic and hexagonal phase, while the post-treated films exhibit the hexagonal phase only (Fig. 3).

This unambiguously means that the CdCl₂ treatment is effective in recrystallizing the CdS film. The crystalline quality and compactness of CdS layer is an important parameter influencing the performance of CdTe/CdS solar cells: nanograins or a metastable crystalline phase (i.e. cubic phase), may enhance the formation of an interdiffused layer at the CdTe/CdS interface which influences the junction transport properties.

2.4. The CdTe layer

The CdTe film is deposited via a CSS technique (Fig. 4) on top of the above described CdCl₂-treated CdS film.

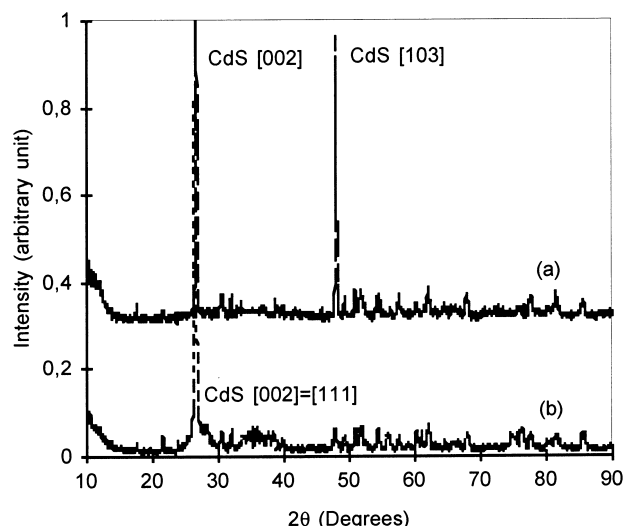


Fig. 3. (a) X-ray spectrum of the CdS layer before the CdCl₂ treatment; (b) X-ray spectrum of the CdS layer after the CdCl₂ treatment. To make the spectrum more legible we eliminated the peaks belonging to the ITO/SnO₂ layer.

First of all, the CdS film is treated in the CSS chamber under 10^{-1} mbar hydrogen pressure and at 350°C substrate temperature for 20 min in order to remove the undesired presence of oxygen compounds (i.e. CdO) and any remaining traces of CdCl₂. After that the CdTe deposition is carried out putting in a graphite crucible a sintered sputtering-like target. This target is a disk shaped with a 3.0 in. diam and is manufactured in this way: a 99.9999% purity CdTe powders provided by Cerac Inc. are placed into a graphite crucible inside an oven. Then under a 50 bar N₂ pressure, the temperature is risen up to 1200°C for 1 h, and therefore, slowly lowered at room temperature. As encapsulant, B₂O₃ is used on top of CdTe. Using a sintered target as a CdTe source, any spitting of CdTe powders is inhibited and the substrate can be directly faced to the source. Besides, a 3 in. diam dimension ensures a very uniform deposition because of its wider size with respect to the substrate. The distance between source and substrate is typically 0.2 cm and

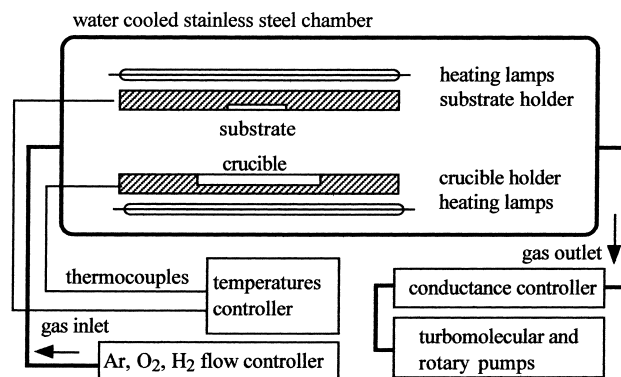


Fig. 4. Schematic diagram of our CSS system.

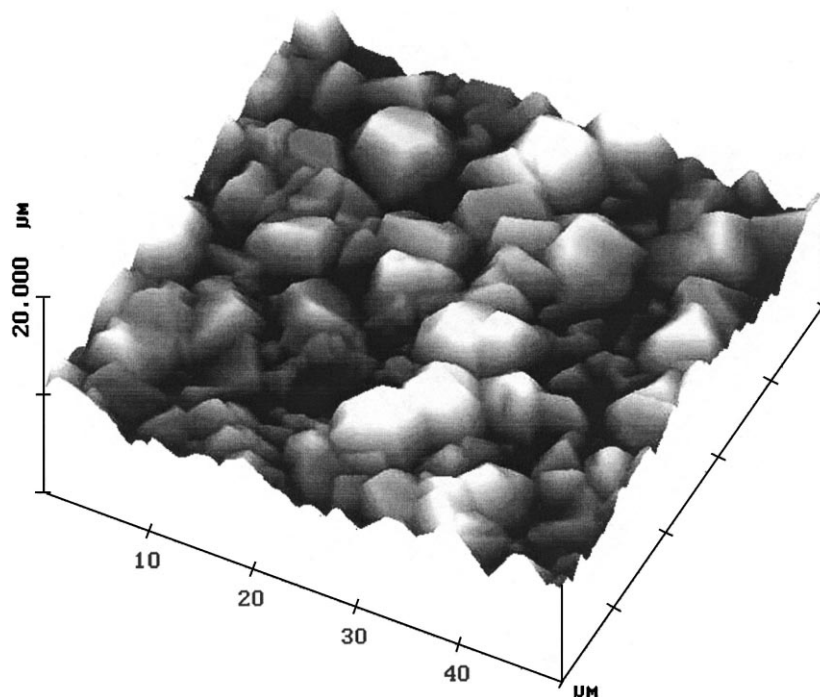


Fig. 5. AFM picture of the CdTe layer deposited at 500°C (on top of the CdCl₂-treated CdS film) by CSS technique with an Ar pressure of 1 mbar and 650°C source temperature. Average grain size $\approx 10 \mu\text{m}$.

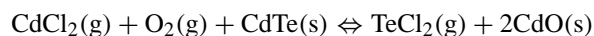
the temperature of source and substrate are 500 and 600°C, respectively. The deposition, is normally carried out in an Ar+O₂ atmosphere. A typical pressure during the deposition is 1 mbar and the content of oxygen is 1%. The role of O₂ is that to slow down the CdTe growth to allow the CdTe to grow with a smaller grain size and to have a better coverage of the CdS film. With these parameters a 5 μm thick CdTe film can be deposited in 5 min. The results of the AFM analysis on the surface of CdTe films are depicted in Figs. 5 and 6. In particular, a fast Fourier analysis has indicated that the average grain size changes from 10 μm for the film grown in Ar only, to 2–3 μm for the film grown with Ar+O₂.

The CdTe film, covered by 0.3–0.5 μm thick CdCl₂ layer, is then treated in air for 20 min at 420–430°C. This treatment is needed in order to remove the structural defects and nanograins in the CdTe film and possibly to dope it with (V_{Cd}–Cl)[–] complexes which behave as acceptor-like dopants.

2.5. The back contact

Contacts for thin film CdTe/CdS solar cells have always been a crucial problem because the presence of elements of the first group of the periodic table of elements limit the lifetime of the device. To solve this problem we use a stable material such as Sb₂Te₃ [5]. This compound is a p^+ type low energy gap (0.3 eV) semiconductor with a resistivity of $10^{-4} \Omega \text{ cm}$. This material is deposited at a substrate temperature of 300–350°C by RF sputtering, using a 99.999%

pure target supplied by Cerac Inc., on top of a CdTe film previously etched in Br-methanol. This chemical etching is necessary in order to remove any oxygen compound and residual CdCl₂ from the surface of the CdTe film. In fact, during the CdCl₂:O₂ vapour heating treatment, CdTe reacts with CdCl₂ and O₂ which results in the production of CdO on the surface of the CdTe grains according to the reaction (at 430°C)



further, CdTe and CdO react with Br₂ in methanol, according to the reactions



The product CdBr₂ is soluble in methanol and water and is removed from the surface by agitation and rinsing. The results is a Te-rich CdTe surface which can react with Sb during the subsequent sputtering deposition of the Sb₂Te₃ back contact, forming a p^+ type layer inside the CdTe film. In fact, the deposition temperature of the Sb₂Te₃ film, sputtered onto the Te-rich CdTe surface, is kept enough high to allow the re-evaporation of Te during the deposition, leaving then a Sb-rich Sb₂Te₃ film. As a consequence, the Sb excess can react with the Te-rich CdTe surface. This p^+ CdTe region ensures an ohmic behaviour of Sb₂Te₃ contact and Sb₂Te₃, being a stable compound, ensures the stability of the devices. Finally, the Sb₂Te₃ is covered by 0.2 μm of Ta or Mo by RF sputtering in the same deposition chamber.

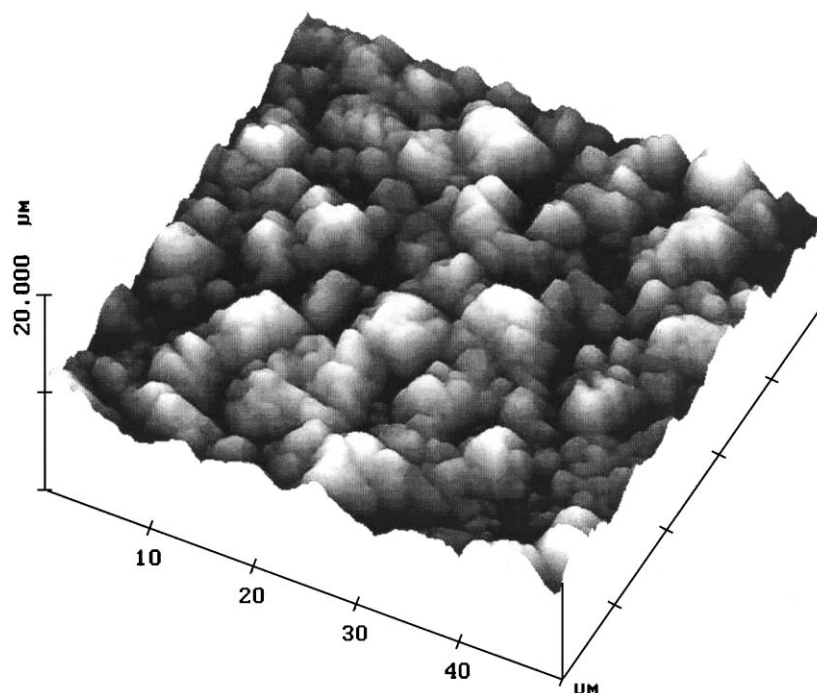


Fig. 6. AFM picture of the CdTe layer deposited at 500°C (on top of the CdCl₂-treated CdS film) by CSS technique with an Ar pressure of 1 mbar+1% O₂ and 650°C source temperature. Average grain size \approx 2–3 μ m.

3. Results and conclusions

Our typical cell is fabricated without antireflecting coating with an area of 0.64 cm² and its characteristics were measured in the dark and under illumination. The J versus V characteristics of the cell, measured under the typical condition of 300 K, 100 mW cm⁻² and AM1.5 making use of a solar simulator supplied by Oriel Inc., are: V_{oc} =858 mV and J_{sc} =23 mA cm⁻² with a fill factor (ff) of 74% corresponding to a total area conversion efficiency of 14.6%. It is in our opinion that the results here reported are the consequence of two important factors which are the role of CdCl₂ in the fabrication of the CdS layer and the Sb₂Te₃ back contact. Since CdS has a lattice mismatch with CdTe of 10%, a true abrupt heterojunction cannot work due to the high amount of interface defects. On the other hand, CdS mixes very easily with CdTe at the high deposition temperature of 500°C and this can remove the mismatch, and consequently, the interface energy states. This is due to the presence of a smooth transition through a mixed compound CdS_{1-x}Te_x. Unfortunately, the cell performance depends strongly on the thickness of this mixed layer. It is here that the role of CdCl₂ treatment of the CdS shows its great importance.

A very fine grained CdS film can easily mix with CdTe giving a too thick CdS_{1-x}Te_x mixed compound. This compound can form a buried homojunction which loses the good performance in photovoltage and photocurrent typical of the heterojunction.

On the contrary, if the CdTe grows on the surface of a CdS layer previously treated with CdCl₂, then the good morphology and compactness of the polycrystalline film does not allow marked mixing, thus favouring the formation of a junction which develops in a few atomic layers still carrying a small amount of interface states. As a consequence of this reason, when we fabricate the device on soda-lime glass making use of a Na-free TCO covered by a CdS layer treated with CdCl₂ we observe a photovoltage consistently over 800 mV and a ff over 72% for all the solar cells prepared [6].

The quality of the Sb₂Te₃ back contact has been investigated by studying the cell performances during a test period of six months, keeping the cell at 60°C under 10 suns in the open-circuit conditions. Under these conditions we did not notice any appreciable degradation of the cell performances, as resulted from the J – V characteristics. During the test period, the cell showed a slight increase of V_{oc} (10–30 mV) while the ff suffered a decrease, which after repeated checks, was never >1%.

In conclusion, with the above described methods, very stable high efficiency CdS/CdTe polycrystalline thin films solar cells could be obtained.

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