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Study of the effect of boron doping on the solid phase crystallisation of hydrogenated amorphous silicon films

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ABSTRACT

Thin-film polycrystalline silicon on glass obtained by crystallization of hydrogenated amorphous silicon (a-Si:H) films is an interesting alternative for thin-film silicon solar cells. Although the solar-cell efficiencies are still limited, this technique offers excellent opportunity to study the influence of B-doping on the crystallisation process of a-Si:H. Our approach is to slowly crystallize B-doped a-Si:H films by solid phase crystallization in the temperature range 580–600°C. We use plasma-enhanced chemical vapour deposition (PECVD) and expanding thermal plasma chemical vapour deposition (ETPCVD) for the B-doped a-Si:H deposition. In this work we show the first in-situ study of the crystallization process of B-doped a-Si:H films produced by ETPCVD and make a comparison to the crystallization of intrinsic ETPCVD deposited a-Si:H as well as intrinsic and B-doped a-Si:H films produced by PECVD. The crystallization process is investigated by in-situ x-ray diffraction, using a high temperature chamber for the annealing procedure. The study shows a strong decrease in the time required for full crystallisation for B-doped a-Si:H films compared to the intrinsic films. The time before the onset of crystallisation is reduced by the incorporation of B as is the grain growth velocity. The time to full crystallisation can be manipulated by the B2H6-to-SiH4 ratio used during the deposition and by the microstructure of the as-deposited a-Si:H films.

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1. Introduction

Photovoltaic solar cells based on thin silicon films have gained wide interest because of the low material consumption, and light-weight and/or flexible applications. These thin-film silicon solar cells are mostly based on hydrogenated amorphous silicon (a-Si:H), deposited using plasma enhanced chemical vapour deposition (PECVD). This material has a high absorption coefficient due to the disorder, allowing almost full absorption of the visible part of AM 1.5 spectrum for a layer thickness of 1 μm [1]. The performance of these thin-film silicon solar cells decreases after prolonged AM 1.5 illumination as a result of the Staebler–Wronski effect [2]. So far the highest reported stabilized efficiency is 10.1% for a single junction a-Si:H cell [2–5]. For this reason researchers have investigated the manufacturing of solar cells based on thin layers of crystalline silicon (c-Si) [6,7]. This material has a much lower defect density and therefore a reduced recombination rate. Although the absorption coefficient of c-Si is much lower than of a-Si:H, 10 μm film thickness would suffice to absorb the sun radiation with an energy above 1.1 eV [8,9].

Thin layers of c-Si have been obtained using several methods. The most direct way of making thin c-Si layers is by cleaving or sawing casted crystalline silicon from ingots [7]. Alternatively, other methods use the crystallization of amorphous silicon (a-Si) or a-Si:H, in particular laser-induced crystallization (LIC) [10] and solid-phase crystallization (SPC) [10,11] resulting in polycrystalline silicon (poly-Si). Using LIC Dore et al. [12] made c-Si grains with a size of 1 mm wide and 10 mm long for 10 μm thick films, and solar cells were made having a conversion efficiency of 8.4% [12]. Problems using LIC are associated with the control of the heat transfer of the laser light to the silicon layer, in particular for films with thickness of more than 300 nm [13]. Another method for the production of thin-film poly-Si is SPC of a-Si(:H) films. In this method a thin layer of a-Si(:H) is annealed at temperatures in excess of 560 °C [14], leading to the formation of c-Si regions. The annealing temperature can be reduced when the crystallization process is catalysed using a metal, most notably Al. This Al-induced crystallization of a-Si(:H) leads to layers having grain sizes of up to 18 μm [15] and as Al is a dopant in Si, the material is always p-type doped. Gall et al. [15] demonstrated this method making solar cells with an efficiency of 2.7%, but higher efficiencies have been reached for other SPC solar cells. A major drawback of the SPC methods is the low open-circuit voltage, VOC, resulting from a high intragrain defect densities [16]. The defect densities in cast c-Si are often associated with the B-content. However, studies on the crystallization process by SPC have mostly been carried out on intrinsic a-Si(:H) layers or on complete solar-cell stacks. Sharma et al. [17] showed that the crystallization kinetics of intrinsic a-Si:H depends strongly on the hydrogen
concentration and the microstructure of the material, expressed in the microstructure parameter, \( R^* \), obtained from the stretching modes in the infrared absorption spectra of as-deposited films. Faster crystallization was observed for lower values of \( R^* \). The largest average grain size was obtained for material having an \( R^* \) value of about 0.3. The faster crystallisation was induced by a faster onset of crystallisation, the onset changes in two ways: (i) the crystallisation onset time increases with decreasing the medium range order (MRO) for low \( R^* \) values; (ii) for layers with increased disorder (i.e., \( R^* > 0.3 \)) the onset decreases with a further decrease in the MRO of the a-Si:H. This could be induced by nanosized voids collapsing upon hydrogen out-diffusion, leading to a more compact structure during SPC.

Technologies based on CVD allow for doping of a-Si:H films during the deposition process. The great benefit of doping during the deposition is that (depending on the cell design) post crystallization doping is no longer necessary. Olson and Roth [18] described the crystallization process of doped a-Si:H and found that both B and P doping increase the crystallization velocity in epilaxial growth experiments [18,19]. For amorphized compensated intrinsic a-Si:Sn [20,21] showed that the crystallization velocity is dependent on the doping level and not on the dopant atom. Additionall, B doping greatly enhances the diffusion of hydrogen in a-Si:H [22]. Therefore it is expected that the SPC of a-Si:H is influenced by the B doping. The solubility of H in c-Si is in the order of 10^{-16} cm^{-3} [23] while up to 25% H can be present in a-Si:H and therefore full crystallisation requires effusion of H. The H effusion characteristics of a-Si:H are very dependent on the microstructure of the material. In this article we show SPC of B-doped a-Si:H, deposited using PE- or expanding thermal plasma (ETP-) CVD. By varying the deposition conditions we have changed the B doping level and the microstructure of the material. We will show that the microstructure of the as-deposited material is hardly affected by incorporating B in the material, whereas the SPC kinetics become much faster.

This article is organized as follows. In the next section we will discuss the experimental procedures for making the a-Si:H layers and the x-ray diffraction (XRD) characterization. We will also show how we obtain the microstructure parameter, \( R^* \), of a-Si:H that has been deposited on glass. In Section 3 we present the results of in-situ XRD on doped a-Si:H layers having varying dopant concentration and microstructure. This section is followed by the discussion section in which we discuss the results using the Avrami-Johnson-Mehl (AJM) model for phase transition [24–26].

2. Experimental details

Samples have been deposited using two different techniques: Radio-Frequency PECVD at 13.56 MHz and ETPCVD. The PECVD setup has a conventional parallel plate configuration with an electrode distance of 10 mm for the intrinsic deposition chamber and 11 mm for the B-doped deposition chamber. The precursor gases were SiH₄ and H₂. For B-doped a-Si:H, B₂H₆ (2% in H₂) was added to the gas mixture. The layers were deposited using an RF power of 28 mW/cm² and a deposition pressure of 70 Pa. The deposition temperature of the PECVD samples was 180 °C and the layers were deposited at a rate of approximately 0.15 nm/s.

ETPCVD of a-Si:H, a DC Ar–H₂ plasma is created in a narrow channel of a cascaded arc at a pressure of approximately 45 × 10⁻³ Pa. The current in the arc is 40 A. The plasma expands through a nozzle into the deposition chamber and at this point H₂ is injected. B-doped films are made by adding B₂H₆ to the H₂ injected at the end of the nozzle. In the deposition chamber, about 8 cm below the nozzle, SiH₄ is injected into the plasma beam and the a-Si:H film is deposited on a temperature controlled glass substrate approximately 40 cm downstream. The pressure in the deposition chamber is about 20 Pa. The deposition temperature is 350 °C and deposition rates used for these samples are between 0.35 and 0.5 nm/s. The films have a thickness of approximately 300 nm. The temperature difference between the PECVD and the ETPCVD deposition was chosen to correspond to the solar grade material from both techniques.

The as-deposited (doped) a-Si:H layers were examined by Raman spectroscopy using a Renishaw InVia Raman spectrometer with a resolution of 2 cm⁻¹. More specifically attention was paid to the Raman active stretching modes of Si–H vibrations at about 2000 to 2100 cm⁻¹ [27]; see Fig. 1. By determining the relative contributions of the low and high stretching mode, the microstructure parameter, \( R^*_R \), is obtained. This parameter is defined as:

\[
R^*_R = \frac{I_{LSM}}{I_{LSM} + I_{HSM}},
\]

where \( I_{LSM} \) and \( I_{HSM} \) are the integrated intensity of the LSM (HSM) mode. It has been shown that the HSM contribution is associated to Si–H bonding configurations indicative of void-rich material, whereas the LSM contribution is linked to Si–H bonds in divacancies [28].

The a-Si:H films were monitored during the crystallization process by in-situ XRD in two sets of experiments. Earlier we demonstrated that the ex-situ XRD patterns of SPC of intrinsic a-Si:H matched those of a polycrystalline silicon reference [29]. We found that the XRD patterns of both B-doped and intrinsic annealed Si films are similar to the pattern of the reference powder, implying that the grains in the films are randomly oriented. The first experiment consisted of annealing at two temperatures: 580 and 600 °C, in an Anton Paar high temperature chamber HTK 1200 under Ar atmosphere. The samples used in this experiment were intrinsic (PE i and ETP i) or deposited using B₂H₆-to-SiH₄ ratios of 2 × 10⁻⁴ (PE B and ETP B).

The second experiment was carried out at 580 °C and 590 °C in a similar Anton Paar HTK setup. In this second experiment the high-temperature chamber was pumped down to 2 × 10⁻¹ Pa, thereby creating a more controlled atmosphere. The B concentration in a-Si:H influences the H-effusion. For this reason the films with varying doping levels are annealed in vacuum. In earlier experiments (not reported here) we have found no indication of oxygen incorporation in the films during annealing. In this experiment two B-doped PECVD films were annealed at 580 °C and two B-doped ETPCVD films were annealed at 590 °C. The B₂H₆-to-SiH₄ ratios of the PECVD samples were 2 × 10⁻⁴ and 7 × 10⁻⁴ for PECVD 2B and ETPCVD 7B, respectively. The ETPCVD films for the second experiment were made with B₂H₆-to-SiH₄ ratios 1.7 × 10⁻⁴ and 7.3 × 10⁻⁴ (ETP 1.7B and ETP 7.3B, respectively). We assume that the boron concentration in the as-deposited a-Si:H films varies with the B₂H₆-to-SiH₄ ratio [30]. We note that the B incorporation efficiency is possibly different for the two deposition methods.

![Fig. 1. Two parts of a typical Raman spectrum of a-Si:H are shown. The 250 to 850 cm⁻¹ range shows the phonon modes related to the Si–Si bonds of a-Si:H, the 2000–2100 cm⁻¹ region shows the Si–Hₓ bonded low and high stretching modes.](image-url)
In both cases XRD patterns were collected by an automatic powder diffractometer in symmetric geometry, using Copper K\(_\alpha\) characteristic radiation (\(\lambda = 0.154\) nm). The irradiated area of each sample was up to 10 mm \(\times\) 10 mm. The XRD pattern was measured in 4 min for \(2\theta\) varying from 26 to 31°, where the strongest silicon line of the (111) planes is located. A typical measurement is shown in Fig. 2. As a measure for crystallization, the crystalline fraction, \(\chi\), was determined by normalizing the integrated intensity of the (111) line during crystallization with respect to the average integrated intensity of the (111) line of the film after saturation of crystallisation occurred. This fully crystallized film will be referred to as the material with crystalline fraction \(\chi = 1\). After annealing Raman spectroscopy was used to confirm that the films were indeed completely crystallized.

3. Results

Before the crystallization experiments, the as-deposited (B-doped) a-Si:H layers were first characterized using Raman spectroscopy, specifically focusing on the Si–H\(_2\) stretching modes. Raman spectroscopy was also used to detect the presence of any crystalline phase in the as-deposited films and we found that all as-deposited films were amorphous. A typical Raman spectrum is shown in 1. For layers deposited using ETPCVD no strong correlation between B\(_2\)H\(_6\)-to-SiH\(_4\) ratio and \(R^*_R\) was observed. We found that \(R^*_R\) is to a large extent determined by the deposition temperature: at low deposition temperatures the \(R^*_R\) of the PECVD samples showed a slight increase with increasing B\(_2\)H\(_6\)-to-SiH\(_4\) ratio. The \(R^*_R\) of the ETPCVD samples deposited at low temperatures is highest, followed by the low temperature PECVD samples, high temperature ETPCVD samples, and the lowest \(R^*_R\) values were observed for the high temperature PECVD samples. We conclude from these results that the microstructure is therefore strongly related to the deposition technique and temperature. For annealing experiments and in-situ XRD analysis we selected samples with varying \(R^*_R\) deposited at different B\(_2\)H\(_6\)-to-SiH\(_4\) ratios.

In Fig. 3 examples of the time evolution of the crystalline fraction, \(\chi\), are shown for intrinsic and B-doped a-Si:H films deposited with ETPCVD and annealed at 580 °C, and deposited with PECVD and annealed at 600 °C. For all films \(\chi\) follows the typical S-shape that characterizes the crystallization of a-Si:H. Intrinsic films deposited by ETPCVD and PECVD show similar crystallisation kinetics for annealing at 600 °C. The onset of crystallisation of the PECVD sample, which has a larger \(R^*_R\), is slightly later than for the ETPCVD and the slope of the S-curve is smaller. The slight differences between the PECVD and ETPCVD crystallization curves are amplified in the SPC treatment at 580 °C, for which we observe that the crystallisation of the ETPCVD
film is now much quicker than that of the PECVD film. Sharma et al. [17] showed that the total crystallization time was shorter for intrinsic ETPCVD a-Si:H films with smaller \( R^* \). The reduction of the total crystallisation time was largely due to a reduction of the onset time to crystallisation, \( \theta \), with a decrease of \( R^* \). This \( R^* \) dependence of the crystallization behaviour is observed when we compare the crystallization of our intrinsic ETPCVD sample with an intrinsic PECVD sample. This indicates that the influence of \( R^* \) on the crystallisation of intrinsic a-Si:H films deposited by PECVD is similar to that of films deposited by ETPCVD.

The \( R^* \) of the as-deposited intrinsic PECVD samples is higher than that of the intrinsic ETPCVD samples. The samples deposited with a \( \text{B}_2\text{H}_6 \)-to-SiH\(_4\) ratio of \( 2 \times 10^{-4} \) have a lower \( R^* \) than the intrinsic samples deposited by the same technique. The most important observation from Fig. 3 is that the onset time for crystallisation is reduced when B is incorporated into the film. In addition, the slopes of the crystallisation curves become steeper when \( \text{B}_2\text{H}_6 \) is added to the gas mixture.

From the XRD measurement results it turns out that the onset of crystallization for the PECVD sample annealed at 600 °C occurs before the annealing temperature has been reached. Although the slope of the ETPCVD sample is slightly steeper than that of the PECVD sample, the overall crystallization time is smaller for the PECVD sample due to the short crystallization onset time. The experiment conducted at 580 °C shows a faster onset of crystallisation, like at 600 °C, but in this case the slope is also steeper for the PECVD sample crystallisation curve compared to that of the ETPCVD sample. We conclude that the crystallization is faster when the samples are B doped and that the effect of B doping on the crystallization time is stronger for PECVD samples than those for ETPCVD samples.

In the second experiment the S-shape results of the \( \chi \) are similar to the results of the first experiment, but the time scale is slightly different. The difference is most likely caused by differences between the setups. Increasing the \( \text{B}_2\text{H}_6 \)-to-SiH\(_4\) ratio leads to a faster onset of crystallisation, more strongly for the ETPCVD samples than for the PECVD samples. The slope of the crystallisation process increases with increasing \( \text{B}_2\text{H}_6 \)-to-SiH\(_4\) ratio. The effect is more pronounced for the PECVD samples. A strong reduction in the time to crystallisation saturation is observed for both techniques.

4. Discussion

In the S-shaped crystallization curves we distinguish two separate parts: (i) the period until the onset of crystallization, and (ii) the curve from the onset of crystallisation until crystallisation saturation (full crystallisation). The time to full crystallisation is affected by the onset or retardation time and the slopes of the crystallization curves. In order to quantify these aspects the measured crystalline fractions are fitted using the AJM model [24–26,31]. Avrami, Johnson and Mehl [24–26,31] used a phenomenological approach to develop an expression for the crystalline fraction. The AJM description can be applied to many kinds of nucleation. In fact the same equations can be constructed from a classical model for nucleation of a solid from a liquid or gas phase [32]. The basic assumption of this model is that no nucleation or growth occurs during the retardation or effective lag time, \( \theta \), and that any misfit strain is negligible. Experimentally, \( \theta \) is related to the minimum detectable grain size or crystalline material volume and is therefore dependent on the measurement technique. In the model, the nucleation rate is defined as the increase of grain density per unit time and is assumed to reach steady-state value (\( l_i \)) when \( t = \theta \) [31]. The grain growth rate, \( v_g \), is assumed to be time independent. With this assumption the crystallized volume fraction, \( \chi \), as function of annealing time can be expressed as:

\[
\chi(t) = 1 - \exp \left( -\frac{(t-\theta)^4}{\tau_c^4} \right).
\]  

In here \( \tau_c \) is the crystallization time, defined as:

\[
\tau_c = \left( \frac{3}{n_{\text{fl}}R_{\text{fl}}^3} \right)^{1/4},
\]

where \( n_{\text{fl}} \) is the film thickness. The grain growth rate \( v_g \) is directly related to the jump rate of atoms at the surface of a grain [33,34]. \( l_i \) and the \( v_g \) are typically described by Arrhenius type equations. However, often \( \tau_c \) is simplified with a single Arrhenius equation with an associated activation energy of SPC (\( \dot{E}_{\text{SPC}} \)) [35]. In a similar fashion an Arrhenius equation is often used to evaluate the activation energy of the onset time to nucleation, \( \theta \). The results of this analysis are presented in Table 1.

As XRD is only sensitive to the crystalline phase, the assumptions of steady-state nucleation and time-independent grain growth rate cannot be confirmed directly. From literature reports B is known to increase \( v_g \) by a factor of 10 to 25 for epitaxial growth of silicon films [18,19,36]. We assume that such a large increase in \( v_g \) and no change in \( l_i \), then according to the AJM model, \( \tau_c \) should decrease by 82 to 91%. The decrease observed for our doped films is in between 45 and 76%, implying that \( l_i \) of the B-doped films is lower if the assumption of a large increase in \( v_g \) is correct. A difference in \( l_i \) between the B-doped and intrinsic samples should result in a difference of the width of the (111) diffraction line, as described by Scherrer [37]. For an infinite crystal the number of reflection planes is infinite and therefore the diffraction line is in fact a line. For small crystallites the number of reflection planes is restricted, resulting in a broadening of the (111) diffraction line. This width is expected to be smaller for lower \( l_i \) values. In we show the development of the (111) relative width, defined as the width-to-integrated intensity ratio, as a function of crystalline fraction \( \chi \). From this figure we can see that for all samples the relative width of the (111) initially increases (\( \chi < 0.1 \)) and then decreases with \( \chi \). According to Sharma et al. [17] annealing of intrinsic ETPCVD samples with a larger \( R^* \) results in films with a larger grain size. As the \( R^* \) of the intrinsic PECVD samples is larger than those of the intrinsic ETPCVD samples it is reasonable to expect a lower nucleation rate and therefore smaller width of the (111) diffraction line, as we observe in Fig. 3. This observation supports the idea that the crystallization of intrinsic a-Si:H films deposited by PECVD are affected by \( R^* \) in a similar way as ETPCVD films. The observation indicates that the grain density in the intrinsic PECVD samples is smaller than that in the ETPCVD samples.

The difference between the expected and determined \( \tau_c \) due to an increase in \( v_g \) we think that the \( l_i \) values of the B-doped samples are smaller than those of the intrinsic samples. These smaller \( l_i \) values result in a decrease of the diffraction line width of the B-doped samples. For a given annealing temperature the absolute diffraction line width of the B-doped ETPCVD films is equal to that of the intrinsic ETPCVD films. The ETPCVD samples annealed at 600 °C have slightly smaller absolute and relative width than those annealed at 580 °C, implying a lower grain density. No difference between the B-doped and intrinsic ETPCVD results is observed. This indicates that the grain density of the B-doped samples is similar to that of the intrinsic samples made by ETPCVD. The only detected difference is a dependence of the grain density on the annealing temperature.

Comparing B-doped to the intrinsic PECVD films, is more complex. The B-doped PECVD sample annealed at 580 °C shows a larger relative width than the intrinsic PECVD sample, in contrast to our expectations outlined above. The reverse is observed for the B-doped PECVD sample annealed at 600 °C, which shows a smaller relative width than the intrinsic PECVD sample. Only one set of samples showed a decrease in the relative width with B-doping, the PECVD sample annealed at 600 °C. This leads us to conclude that the differences in \( \tau_c \) of the intrinsic and B-doped samples, deposited by both techniques, are not caused by a decrease in \( l_i \). The difference in \( \tau_c \) of the intrinsic and B-doped samples is the result of a decrease in \( v_g \), which is smaller than the increase expected from our literature study. The observed decrease in \( \tau_c \) could be related to the degree of B-doping. The differences between the crystallisation
of the B-doped ETPCVD and B-doped PECVD films can be influenced by \( i_a \) and/or \( \nu_f \). We therefore conclude that the variation of \( i_a \) is not the main factor for the difference in crystallisation behaviour of the intrinsic and doped samples.

In order to study the observed differences between the B-doped ETPCVD and PECVD films in more detail, a second experiment was carried out in which the effect of increasing B-doping is investigated. With this experiment we attempt to shed more light on the differences between the values of \( \nu_f \) described in literature reports and our findings. Olson and Roth [18] described that at very high B concentrations the decrease of the grain growth rate, \( \nu_f \), was diminished by B precipitates or B–Si complexes. The crystallisation curves of four additional samples are measured and analysed using the AJM model and the results are presented in Fig. 4 and Table 1. By increasing the B2H6-to-SiH4 ratio to \( 7 \times 10^{-4} \) we obtained lower \( \tau_c \) values, indicating a further increase of \( \nu_f \). The PECVD film 7B shows a decrease of \( \tau_c \) with respect to 2B of 51% (for annealing at 580 °C) and the ETPCVD film 7.3B a 19% decrease with respect to 1.7B (for annealing at 590 °C).

The second experiment also provides information on the influence of \( R^*_f \) on \( \tau_c \) and \( \theta \). Two samples were selected having similar \( R^*_f \), but different deposition techniques. These samples were annealed at 580 °C and 590 °C. Notably the crystallisation curves of the PECVD 2B sample annealed at 580 °C and the ETP 1.7B annealed at 590 °C look very similar. These two curves are used as a reference to observe changes in the crystallisation curves when: (i) the B2H6-to-SiH4 ratio is increased from \( 1.7 \times 10^{-4} \) and \( 2 \times 10^{-4} \) to \( 7 \times 10^{-4} \) and \( 7.3 \times 10^{-4} \), and (ii) the \( R^*_f \) of the PECVD sample is increased and the \( R^*_f \) of the ETPCVD sample is reduced. The results show that increasing the B2H6-to-SiH4 ratio shortens \( \theta \) and \( \tau_c \). A decrease in \( R^*_f \) should lead to reduction of the incubation time \( \theta \) according to Sharma et al. [17]. The \( R^*_f \) of PECVD 7B and the ETP 7.3B samples is reduced in both cases, showing the influence of B. The degree to which \( \theta \) is reduced is affected by the \( R^*_f \) of the samples. The reduction in \( \theta \) is smaller for the PECVD sample for which the \( R^*_f \) increases, and larger for the ETPCVD samples for which \( R^*_f \) decreases.

5. Conclusion

We have shown that B doping reduces the onset of crystallization of a-Si:H and the crystallization time. From the analysis of the XRD results we conclude that B enhances the grain growth rate of the B-doped a-Si:H films, but that the effect of the B on the nucleation rate is limited. The extent of the enhanced grain growth rate due to B doping is controlled by the B2H6-to-SiH4 gas flow ratio, for both PECVD deposited films and ETPCVD deposited films. In addition to the influence of B, we conclude that also \( R^*_f \) influences the crystallisation process. For both intrinsic PECVD and ETPCVD samples increasing \( R^*_f \) increases the onset time to crystallization [17]. The influence of \( R^*_f \) is also present in the crystallisation process of the B-doped a-Si:H films deposited by ETPCVD and PECVD.

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