SiHx film growth precursors during high-rate nanocrystalline silicon deposition

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Thin films of nanocrystalline silicon (nc-Si:H), also referred to as microcrystalline silicon, are attracting a great deal of attention for the use in thin film transistors for active matrix displays and in solar cells due to the enhanced electronic performance and stability of the material over amorphous silicon (a-Si:H). The importance of atomic hydrogen H during the preparation of these films from a gas mixture of SiH₄ and H₂ by plasma or hot-wire based deposition techniques is well recognized. However, on the importance of the different silane radicals for film growth it has only been speculated. Commonly, it is assumed that SiH₃ is the key radical for nc-Si:H film growth, similar to the case of a-Si:H. Yet direct experimental information on the gas phase densities of the different silane radicals under nc-Si:H deposition conditions is still lacking.

To obtain insight into the role of the different silane radicals under nc-Si:H conditions, we have measured these radicals employing the cavity ringdown technique following our previous work under a-Si:H conditions in the expanding thermal plasma (ETP). We report on the measured absolute densities of Si, SiH, and SiH₃ for different H₂ dilution ratios spanning the region from a-Si:H to nc-Si:H film growth. Experimental conditions yielding high deposition rates have been chosen as these are currently of prime importance for industry as generally recognized. On the basis of the densities measured, we address the importance of the different silane radicals during nc-Si:H growth and it will be revealed that SiH₃ is indeed the dominant silane radical for nc-Si:H films. However, contrary to a-Si:H conditions, the contribution of lower silane radicals such as Si and SiH becomes very significant under nc-Si:H conditions in line with expectations and indirect indications reported in the literature.

The experiments have been carried out in a remote plasma reactor for high-rate deposition of high-quality a-Si:H: the expanding thermal plasma (ETP). This technique, which uses an upstream generated Ar-H₂ plasma to dissociate SiH₄, is also capable of depositing nanocrystalline silicon at high rates (up to 3 nm/s) under high H₂ dilution conditions. In the present work, experiments are reported as a function of the H₂ dilution ratio of SiH₄, R=H₂ flow/SiH₄ flow. In these experiments the SiH₄ flow has been varied while the H₂ flow was fixed at 30 SCCS (standard cubic centimeter per second). Also some experiments were carried out with 10 SCCS H₂ yielding optimized a-Si:H. The pressure in the reactor was maintained at ~150 mTorr (~20 Pa) while other experimental conditions were equal to those reported in Refs. 17 and 18.

The cavity ringdown measurements took place relatively close to the substrate (at 3.6 cm) using the experimental arrangement and procedures described extensively in our previous work. SiH₃ has been measured at the broadband X ← A₁ transition at a wavelength of ~250 nm and its density has been quantified by the cross-sectional data reported by Baklanov and Krasnoperov. The ground state Si density has been determined from measurements at the 3P_0,1,2 ← 1P_0,1,2 transitions at 250.7, 251.4, and 251.9 nm using the Einstein absorption coefficients reported. The total SiH density has been deduced from measurements of the Q(11.5) rotational line of the SiH A ← X ²Π band at ~414 nm using information on the cross section and partition function available in LIFBASE.

Figure 1 shows the deposition rate and Raman spectra of the films obtained under the conditions that were investigated by cavity ringdown spectroscopy yielding the Si, SiH, and SiH₃ radical densities in the plasma, as shown in Fig. 2. Figure 1 reveals that the deposition rate decreases for increasing dilution ratio R which is varied by changing only the SiH₄ flow at a fixed H₂ flow of 30 SCCS. The Raman spectra reveal that a transition from amorphous to nanocrystalline silicon takes place between R=43 and R=60. The crystallinity of the films increases from 59% at R=60 to 77% at R=200. The density of the silane radicals in Fig. 2 shows only a gradual change as a function of the dilution ratio R. Also data for low R values (R<10, H₂ flow is 10 SCCS), as
typically used for optimized a-Si:H films, have been included in this plot to reveal the trend in the densities over a large dilution range. The figure reveals that the SiH₃ radical is the dominant silane radical in the plasma for all conditions, independent of amorphous or nanocrystalline silicon growth. Under the nc-Si:H conditions, the SiH₃ density is in the order of 10¹² cm⁻³ and this density increases considerably when going to lower dilution ratios. For these lower dilution ratios more SiH₄ is available for dissociation yielding a higher SiH₃ density and also a higher deposition rate compared to the nc-Si:H conditions. Under the nc-Si:H conditions, the SiH₄ consumption reaches virtually 100% as revealed by mass spectrometry.

The densities of Si and SiH are around 10¹¹ cm⁻³ for the nanocrystalline silicon conditions and all other high dilution ratios with R>20. These densities decrease when going to the optimized a-Si:H conditions with R<10 and especially the Si density goes down drastically and reaches even densities below 10⁹ cm⁻³. Under the ETP “standard” conditions with R=10, the SiH and Si densities are 5×10¹⁰ cm⁻³ for SiH and 10⁹ cm⁻³ for Si, corresponding with an estimated contribution of SiH and Si to a-Si:H growth of ~2% and ~0.2%, respectively. From Fig. 2, it is therefore clear that the contribution of SiH and Si to nc-Si:H film growth is much higher. Apart from the difference in density between the different radicals, also the difference in sticking probability of the radicals on the silicon surface has to be taken into account when considering the contribution of the radicals to film growth. Si and SiH have a sticking probability very close to unity while the sticking probability of SiH₄ is at least a factor of 3 lower. This means that the relative contribution of SiH and Si to nc-Si:H film growth compared to SiH₃ is even higher than suggested by Fig. 2. Consequently, a contribution of at least 5% at R=60 (deposition rate: 2.9 nm/s; crystallinity: 59%) can be estimated for both Si and SiH while this contribution will go up to at least 15% for R=200 (deposition rate: 1.5 nm/s; crystallinity: 77%). The contribution to nc-Si:H film growth needs to be balanced to 100% by SiH₃ radicals as well as other radicals and ions such as SiH₂. For this latter radical, for example, it is expected that its contribution to film growth will also go up when going from a-Si:H to nc-Si:H growth conditions on the basis of the plasma reactions discussed next.

The increasing importance of the hydrogen poor radicals such as Si, SiH, and probably also SiH₂ under nc-Si:H conditions can be related to two effects. First of all, abundant atomic H is available under SiH₄ depleted conditions such that hydrogen abstraction from SiH₃ (and subsequently from the lower silane radicals produced) by H can continue to take place. A second reason is that the gas phase loss of radicals such as Si and SiH due to reactions with SiH₄ is tremendously reduced under the SiH₄ depleted conditions. SiH and particularly Si are very reactive with SiH₄ [reaction rates are 5×10⁻¹¹ cm³ s⁻¹ (Refs. 10 and 26) and 3×10⁻¹⁰ cm³ s⁻¹, respectively] and will not easily survive under conditions with abundant SiH₄, i.e., under a-Si:H conditions. For example, for a typical SiH₄ density of 10¹⁴–10¹⁵ cm⁻³ the lifetime of these radicals is far less than 1 ms which is a typical diffusion time of radicals to the substrate/reactor walls. This gas phase loss channel will be virtually absent under the SiH₄ depleted nc-Si:H conditions, leading to higher Si and SiH densities just in front of the substrate.

In summary, the densities of different silane radicals in the expanding thermal plasma have been measured revealing that the SiH₃ density is at least an order of magnitude higher than the Si and SiH densities for all H₂ dilution ratios investigated. Although the exact density of the radicals and their flux to the substrate depend on the plasma source and its operating conditions such as pressure, these measurements provide more evidence that nanocrystalline silicon film growth is generally also mainly governed by SiH₃ radicals, similar to a-Si:H. The surface reactions leading to film growth can therefore be described in terms of SiH₃ and H reactions for a large extent. However, the contribution of lower silane radicals also becomes significant for high H₂ dilution ratios and cannot simply be neglected in every aspect of nanocrystalline silicon growth.
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25The sticking probability of SiH₃ is lower than or equal to its surface reaction probability. The SiH₃ surface reaction probability is ~0.3 for a–Si:H and is expected to be similar in magnitude for nc-Si:H.