PROPERTIES OF AMORPHOUS SiC:H ALLOYS WITH LOW CARBON CONTENT.

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Abstract

In this paper we report the properties of a-SiC:H films with low carbon content deposited from SiH_4:CH_4:H_2 gaseous mixtures. In case of films deposited without H_2 dilution, carbon incorporation mainly as CH_3 groups was determined. Increasing H_2 dilution was found to induce a selective incorporation of radicals that affects the density of C-H bonds, thus reducing the mean number of carbon bonded hydrogen atoms per carbon atom. This leads to a more compact material with a reduced density of voids, which is believed to be the main reason for the improvement of the electronic properties of films.

Keywords: Amorphous semiconductors, silicon - carbon alloys.

INTRODUCTION

Hydrogenated amorphous silicon carbon alloys (a-$Si_{1-x}C_x$: H) have attracted considerable interest over the last years both due to their promising applications as variable band gap semiconductor and to fundamental physical aspects. However, a major problem of this material is the rapid deterioration of its electronic properties when carbon concentration is increased. This fact was attributed by other authors to the presence of microstructure, which was related to the incorporation of bond terminating CH_3 groups into the films [1,2]. A few years ago, Matsuda et al. showed that hydrogen dilution of gases is a powerful way of improving the electronic properties of this material and related this fact to the increased diffusion coefficient of radicals on the surface of the growing film[3]. Recently, Baker al. reported on a systematic study of the effect of hydrogen dilution on a-SiC:H films confirming that better electronic and structural properties are obtained [4]. In a previous study, it was shown that a correlation exits between the photoconductivity of a-SiC:H, the concentration of CH_3 radicals, total hydrogen content and the amount of microstructure presented by the material, thus permitting the conclusion that H_2 dilution improves the electronic properties basically because a more compact material is obtained [5]. In spite of these facts, the form which carbon actually is incorporated into the material is subject of a considerable debate and still remains an open question [1,6]. In the present work, we further investigate the properties of a-SiC:H films with low carbon content.

EXPERIMENTAL

Amorphous a-SiC:H films were produced in a capacitively coupled RF glow discharge reactor from SiH_4:CH_4:H_2 gaseous mixtures. Substrate temperature was 250°C and RF power density 0.1 W/cm^2 at 13.6 MHz. Two sets of sample were prepared. In the first one, the flows of SiH_4 and CH_4 were kept fixed to produce samples with constant optical gaps (1.92 ± 0.02 eV), while hydrogen fraction ($[H_2]/[SiH_4] + [CH_4]$) was varied from zero to 8.0. In the second set, hydrogen dilution was employed and the ratio of the flows of SiH_4 and CH_4 was varied. In both cases total pressure was kept fixed at about 0.5 mBar by properly adjusting the pumping speed. High resistivity crystalline silicon and Corning 7059 glass substrates were used.

Samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) in a Nicolet 740 spectrometer. Hydrogen content of the samples was measured either by Elastic Recoil Hydrogen Detection (ERHD) or Hydrogen Effusion (HE) techniques, both methods giving similar results. ERHD was done by impinging energetic alpha particles from a van de Graff accelerator onto the samples and detecting protons in the forward direction. For HE experiments,

samples were placed inside a quartz tube, pumped down to 10^{-7} torr and gradually heated up to about 1000°C while the partial pressure of H_2 was monitored by a quadrupole mass analyzer. Carbon content was obtained by Auger Electron Spectroscopy (AES) by measuring the Si LVV (90 eV) and C KVV (270 eV) peaks using a crystalline SiC sample as calibration standard.

RESULTS AND DISCUSSION

Figure 1 (solid circles) shows that total hydrogen concentration of the samples is greatly reduced when hydrogen is added to the discharge, in accordance to our previous observation [5]. Figure 1 (open circles) also shows the values of the density of Si - H bonds N_{Si-H} obtained from the integration of the 640 cm^{-1} SiH_n wagging mode infrared absorption peak [7]. As one can observe N_{Si-H} is not affected by hydrogen dilution in accordance to the results obtained by Tsai et al. in the case of a-Si:H [8]. If one now assume that hydrogen atoms are bonded either to silicon or to carbon, then these results lead to the conclusion that hydrogen dilution reduces the total hydrogen content of the films by affecting the incorporation of hydrogenated carbon radicals.

The explanation of this behavior is directly related to the existing controversy about the form of carbon incorporation into the material. Two opposite points of view are found in the literature in case of methane based films deposited with low RF power density: (i) carbon is incorporated substitutionaly into the bulk of the material and only a small fraction is found in the form of CH_3 groups [1], and (ii) carbon is incorporated primarily as CH_3 radicals [6].

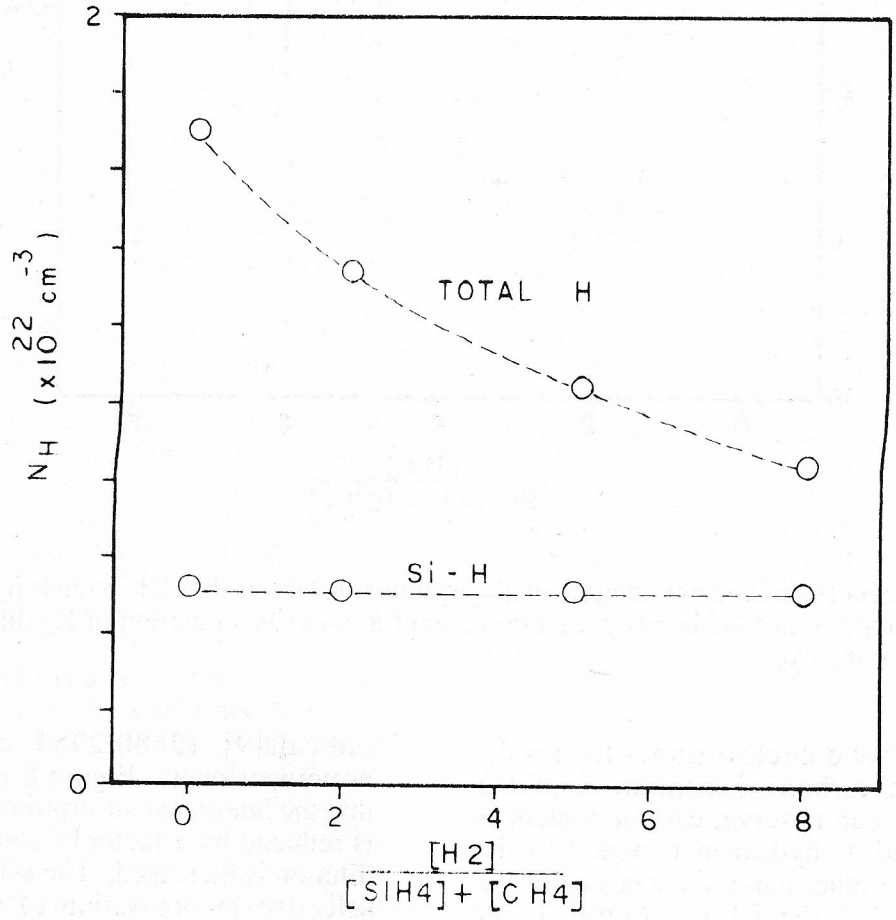

Fig 1. ERHD total hydrogen concentration (solid cycles) and density of Si-H bonds (open circles) as a function of H_2 dilution. Dashed lines are guides to the eye.

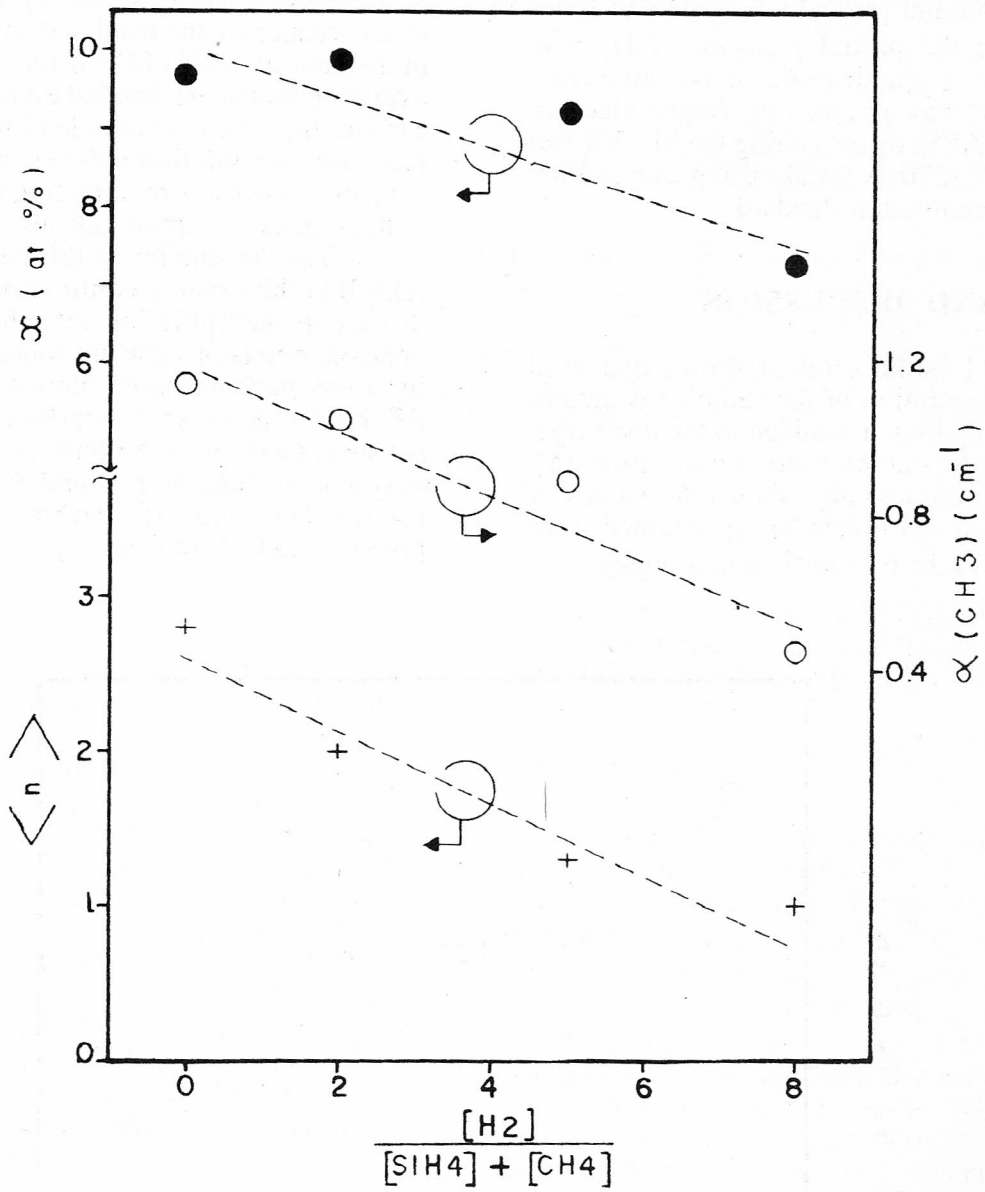

Fig 2. Carbon content (solid cycles), integrated absorption constant of the CH_3 stretching mode (open circles) and mean number of C-H bonds per carbon atom (crosses) as a function of H_2 dilution. Dashed lines are guides to the eye.

Figure 2 (solid circles) shows the results obtained for the carbon concentration of the samples. As one can observe, carbon content is slightly decreased as hydrogen is added to the discharge. On the other hand, the analysis of the high energy side of the FTIR spectra of our samples, showed that those peaks commonly attributed to the stretching mode of CH_3 radicals[9] (2880/2950 cm^{-1}) are the most prominent ones. Figure 2 (open circles) shows that the integrated absorption constant of this band is reduced by a factor of about 3 when hydrogen dilution is increased. These results point toward a selective incorporation of radicals induced by hydrogen dilution and lead to the conclusion the form of carbon incorporation into the material may depend strongly on the hydrogen partial pressure

in the discharge. In order to check in a quantitative way the above conclusions we made an estimation of the mass density of our samples by interpolating the data of both Mahan [1] and Sotiropoulos[10]. Although obtained from films deposited somewhat different deposition conditions, these data agree well with each other in the range of low carbon content, thus encouraging us to proceed in this way. From the values thus obtained and our data, the atomic density of carbon N_c was calculated. Then the mean number of C-H bounds per carbon atom $<n>=N_{C-H}/N_c$ was found, using $N_{C-H}=N_H-N_{Si-H}$. As shown in figure 2 (crosses) our results indicate that carbon is incorporated primarily as CH_3 in case of films deposited without hydrogen dilution, in accordance to the results of Solomon [6]. However, our results seem to be more reliable since we have determined <n> from the density of C-H bounds and not from the total hydrogen content. Furthermore, our results also show that effect of hydrogen dilution is to reduce the incorporation of the more hydrogenated carbon radicals reducing <n> gradually to about only 1.0 in case of films deposited with high dilution. It may be argued that the mass density of our samples may differ somewhat from those of the cited references since a more compact material is expected as a result of hydrogen dilution. However, this would affect <n> only slightly and therefore the qualitative conclusions obtained here would not be changed.

According to Matsuda and Tanaka the effect of H_2 dilution is to increase the surface mobility of absorbed radicals, thereby increasing the probability for them to diffuse to energetically favorable sites[3]. In view of the present results we suggest that as a result of this process the incorporation of CH_3 radicals decreases because less hydrogenated radicals are more tightly connected to the network than CH_3 ones, due to a larger of Si-C bonds. The previous observation of an increased absorption constant for the SiC IR vibrational mode supports this view[5].

It still remains to be explained why the stretching mode of CH_3 groups is the most prominent one in the high energy side of the IR spectra of methane based films with low content. This is the case for most of the results found in the literature and also for all of our samples, even those deposited with high H_2 dilution. Two possible explanations may be given for this fact. The first one would simply be that the density of CH_3 groups could be larger than in case of CH_2 or CH, and therefore the observed effects would be due to an increasing density of carbon atoms tetrahedrally bonded to the silicon network. A second explanation may also be given taking into account that a reduction in the oscillator strength of the C-H stretching modes ($°_{C-H}$) may occur as the number of Si atoms back bonded to C is increased[11]. Although qualitatively reasonable this explanation does not take account the effect of the local field, which in case of a solid is different from the applied field and could affect the value of $°_{C-H}$, thus impeding one to make quantitative predictions and decide between the two possibilities. Further work is still needed in order to elucidate this issue.

The reduction of the number of C-H bonds per carbon atom and the consequent improvement of the network connectivity have important consequences to the structure of the material. The most important one is the decrease of density of voids that can be observed by both IR and HE experiments. In the first case, a decrease of 2070 cm^{-1} Si-H stretching mode and increase of the 2000 cm^{-1} one more observed as H_2 dilution is increased. This indicates that the density of Si-H bounds at the internal surface of voids decreases and the density of Si-H bounds inside the bulk is increased while the total density remains essentially constant (see figure 1). HE experiments show that two effusion peaks can be observed. The low temperature peak is associated to a void related effusion process while the high temperature one corresponds to the effusion to the hydrogen from compact material[12]. Figure 3 shows as hydrogen dilution is increased bout effusion peaks are reduced indicating that the reduction in the total hydrogen content implies in a reduced density of voids as shown by the low temperature effusion peak. This fact is believed to be the main reason for the improved electronic properties of films deposited with hydrogen dilution[5].

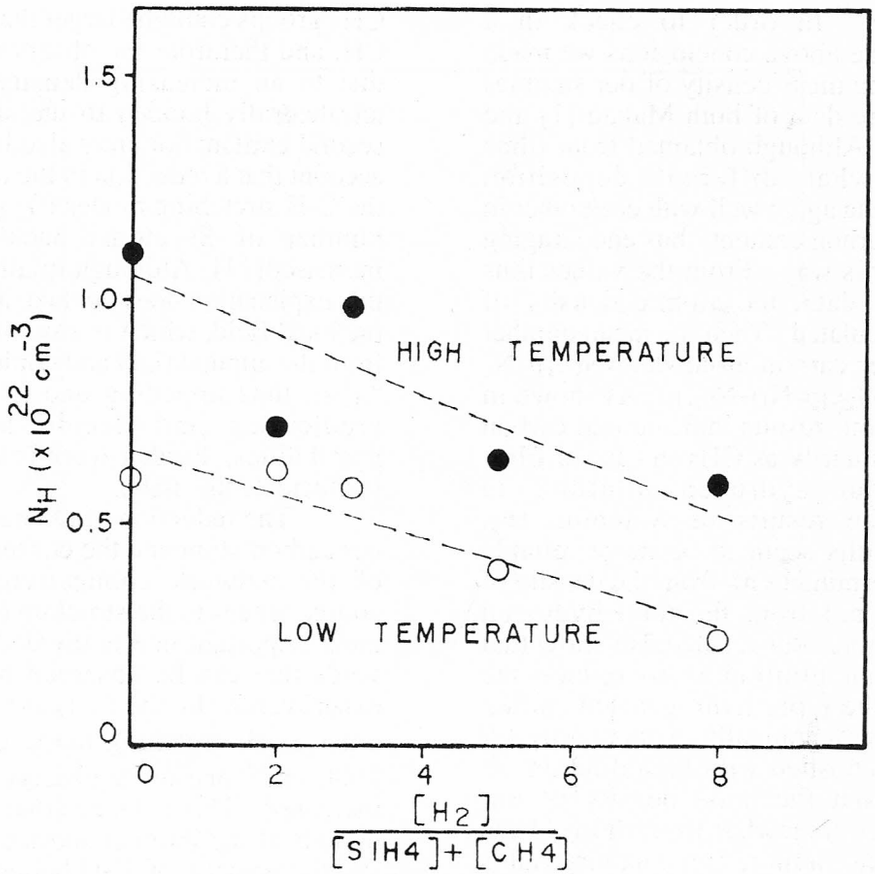

Fig 3. Hydrogen densities in the high and low temperature effusion peaks as a function of H2 dilution. Dashed lines are guides to the eye.

CONCLUSIONS

In summary, carbon incorporation primarily as CH_3 groups was determined for undiluted films. H_2 dilution was shown to induce a selective incorporation of radicals reducing the density of carbon bonded hydrogen atoms. This effect implies in a more compact material with a reduced density of voids.

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