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DEPOSITION AND CHARACTERIZATION OF AMORPHOUS AND MICRO-CRYSTALLINE Si,C ALLOY THIN FILMS BY A REMOTE PLASMA-ENHANCED CHEMICAL-VAPOR DEPOSITION PROCESS - RPECVD

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The RPECVD process has been extended to deposit a-Si,C:H and μc-Si,C:H.The degree of crystallinity in the μc-Si,C:H alloys is lower than in μc-Si:H films deposited under comparable conditions. Attempts to dope μc-Si,C:H alloys indicate that high levels of both B and P doping can promote a transition from μc-Si,C:H to a-Si,C:H. Raman spectra indicate that crystallites in the μc-Si,C:H alloys are Si, while IR measurements show that the amorphous component is an a-Si,C:H alloy.

1. INTRODUCTION

The electrical and optical properties of glow discharge, GD, a-Si,C:H and μc-Si,C:H can be tailored for device applications by varying the concentrations of Si and C. The wider band gaps of a-Si,C:H and μc-Si,C:H relative to a-Si:H and μc-Si:H, respectively, coupled with the ability to dope, have made the Si,C alloys important constituents in high efficiency a-Si solar cells[1], and in electroluminescent devices[2]. We have previously established that device-quality a-Si:H and μc-Si:H can be deposited by RPECVD, and that these films can also be incorporated into devices[3-5]. In this paper, we extend these studies of RPECVD films to the deposition of intrinsic and doped a-Si,C:H and μc-Si,C:H. The amorphous films are produced by remotely exciting downstream injected SiH_4-CH_4 source gas mixtures, and the μc-Si,C:H films are produced by adding H_2 downstream as well. We have deposited n-type and p-type Si,C alloy films by introducing the dopant atom source gases, PH_3 or B_2H_6, downstream from the plasma excitation region. The structural, electrical and optical properties of a-Si,C:H and μc-Si,C:H films have been investigated and are reported below.

2. FILM DEPOSITION

The RPECVD deposition system used in these studies is described elsewhere[3]. The conditions for depositing a-Si,C:H films are essentially the same as those used for device-quality a-Si:H films, except that the C-atom source gas CH_4 is introduced downstream along with the Si-atom source gas SiH_4, and the combined flow of the SiH_4+CH_4 mixture is maintained at a level comparable to the flow of SiH_4 for the a-Si:H depositions. We define the SiH_4 fraction of these gas mixtures as $X = SiH_4/(SiH_4+CH_4)$, and have varied X between 1.0 and 0.33, to deposit a-Si,C:H films that contain up to ~15 at.% C. For the deposition of the μc-Si,C:H alloy films, a flow of 30 sccm of molecular hydrogen, H_2, was added downstream to the SiH_4/CH_4 source gas mixture. For the deposition of doped a-Si,C:H or μc-Si,C:H, the dopant-atom source gases, diborane, B_2H_6, and phosphine, PH_3, were premixed with

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the Si- and C-atom source gases and also injected down-stream.

3. PROPERTIES OF a-Si,C:H and μc-Si,C:H

A series of a-Si,C::H alloy films with different C-atom concentrations has been deposited by varying X between 1 and 0.33. The local bonding in these films was characterized by IR absorption. The spectral features specifically associated with C-atom incorporation have been discussed elsewhere[7]. These IR features include bond-stretching and bending absorptions due to Si-C, CH_3 and C-SiH groups. Each of these spectral features increases in strength as the CH_4 fraction in the source gas mixture is increased, i.e., as X decreases from 1.0 to 0.33.

We have also studied the electrical and optical properties of this same series of a-Si,C:H alloy films. The dark conductivity, the photoconductivity and the effective optical bandgap are essentially the same as those in a-Si,C:H alloy films deposited by the GD method using comparable SiH_4/CH_4 source gas mixtures. The bandgap and photoconductivity data indicate that as X decreases from 1 (a-Si:H) to 0.5, the E_{04} bandgap increases from ~1.90 eV to ~2.25 eV, and the photoconductivity for illumination by white light at ~50 mW/cm^2, decreases from 5.5×10^{-5} S/cm to 8.9×10^{-9} S/cm, both effects similar to the results reported for GD films. E_{04} is 2.05 eV for the undoped X = 0.67 a-Si,C:H.

As stated above, p-type and n-type a-Si,C:H alloy films have been deposited by adding the dopant atom gases to the downstream injected SiH_4/CH_4 gas mixture. The most extensive of these studies have been confined to a single SiH_4/CH_4 source gas mixture, X = 0.67. For the highest diborane doping gas ratio used, (1%), and for X = 0.67, the conductivity of the p-type a-Si,C:H was 1.4×10^{-6} S/cm with an activation energy of 0.46 eV. This conductivity is about a factor of 500 less than what is obtained in a-Si:H for the same doping gas fraction. The decreased dark conductivity is consistent with an increased activation energy: 0.46 eV in a-Si,C:H, and 0.31 eV in a-Si:H. For the highest phosphine doping gas ratio, also (1%), the dark conductivity was 3.5×10^{-5} S/cm with activation energy of 0.41 eV. This is about a factor of 570 less than that of a-Si:H grown from the same relative concentration of PH_3. The decreased conductivity is also in accord with an increased activation energy: 0.41 eV as compared to 0.25 eV. This means that the

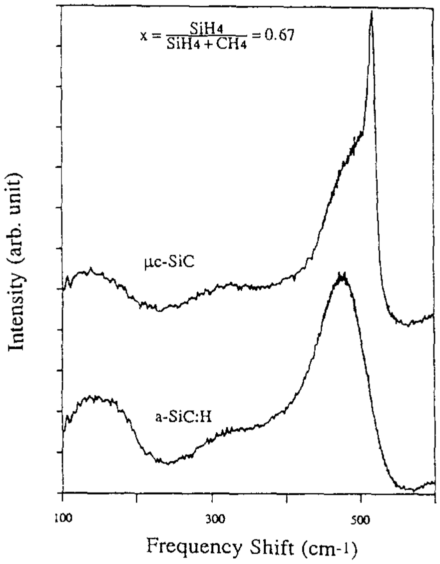

FIGURE 1
Raman spectra of μc-Si,C:H and a-Si,C:H.

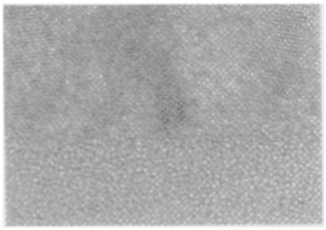

FIGURE 2
TEM micrograph of μc-Si,C:H/SiO_2 interface. The μc-Si,C:H is on top, and the SiO_2 on the bottom.

smaller conductivities for the doped a-Si,C:H as compared to a-Si:H result mostly from the larger activation energies[8], and the conductivity prefactors, which characterize transport in extended states of the conduction and valence bands of a-Si,C:H, are essentially the same as in a-Si:H.

μc-Si,C:H alloy films have been deposited by RPECVD by adding H_2 to the downstream injected SiH_4/CH_4 source gas mixtures. The combined effective flow rate of the SiH_4/CH_4 mixture was maintained 1~2 sccm, and the flow rate of the H_2 was fixed 30 sccm, the same ratio as used for the deposition of the μc-Si films with the highest fraction of crystallinity. The degree of crystallinity in the μc-Si,C:H alloy films has been investigated by Raman spectroscopy (Fig. 1) and transmission electron microscopy (TEM) (Fig. 2). Studies by TEM imaging and Raman scattering indicate a decreased amount of crystallinity in μc-Si,C:H as compared to μc-Si prepared under similar deposition conditions. Raman spectra for μc-Si,C:H, and for a-Si,C:H alloy films deposited on fused silica are displayed in Fig. 1, and show that μc-Si,C:H alloy films exhibit a sharp feature at 520 cm^{-1} that is the same as the sharp crystalline feature found in μc-Si films. This establishes that at least one of the possible crystalline components in these films is Si. The fraction of crystallinity can be estimated from the ratio of the Raman scattering in the crystalline "TO" feature to that in the 470 cm^{-1} "TO" band; for the film shown in Fig.1this is ~10-20%. We have obtained the Raman spectrum over a spectral range from about 100 to 1500 cm^{-1}, and have found no evidence for spectral features associated with crystalline SiC, or with either of the crystalline forms of carbon: diamond or graphite. This means that the C-atoms incorporated into the μc-Si,C:H alloys must then be included in the amorphous material that is interposed between the Si crystallites. This interpretation of the Raman and TEM data is supported by the IR spectra discussed in Ref. 7. Furthermore, by adding additional CH_4 into the source gas mixtures that include H_2, the degree of crystallinity of deposited alloy films decreases. Hydrogenated amorphous carbon films have been deposited under the same deposition conditions but with no SiH_4 in the source gas mixture, and with the flow rate of H_2 maintained at 30 sccm.

TABLE I

PROPERTIES OF Si,C ALLOY FILMS

X	Doping Gas Ratio	Dark Cond. (S/cm)	E_a (eV)
0.67	PH_3, 0.1%	5.6e-2	0.10
0.50	PH_3, 0.1%	1.0e-3	0.22
0.33*	PH_3, 0.1%	6.2e-13	0.91
0.67*	PH_3, 1.0%	1.3e-3	0.23
0.67	B_2H_6, 0.1%	6.3e-4	0.18
0.50	B_2H_6, 0.1%	1.1e-6	0.44
0.33*	B_2H_6, 0.1%	8.2e-10	0.73
0.67*	B_2H_6, 1.0%	1.4e-7	0.56

* these films are amorphous even though they were deposited using H_2

Deposition of heavily doped, p-type and n-type μc-Si,C:H alloy films also has been accomplished by RPECVD, however for a limited set of gas flow conditions. The dopant atom source gas, either diborane or phosphine, was added to the Si- and C-atom source gas mixture at concentrations of 0.1% and 1%, and for X = 0.33, 0.5 and 0.67. Table I summarizes the results of these depositions. Films deposited with 1% *gas phase doping* of the X = 0.67 Si-atom and C-atom source gas mixture were amorphous as determined by analysis of the Raman scattering. Films deposited from 0.1% doping gas mixtures were microcrystalline for X = 0.67 and 0.50, but became amorphous when the silane fraction was further reduced to 0.33. Raman scattering was also the characterization technique used to distinguish between the amorphous and microcrystalline character of these less heavily doped films. We have also studied the properties of undoped Si,C alloy films grown under flow conditions which included 30 sccm of H_2. µc-Si,C:H films were obtained for X = 0.67 and 0.50, but not for X = 0.33. It is interesting, and important to note that the doped and undoped a-Si,C:H alloys that are produced with H_2 dilution of the SiH_4/CH_4 mixtures have properties which are generally different from a-Si,C:H films produced without the H_2 flow. For example, the conductivity of p-type a-Si,C:H films deposited with a gas phase doping fraction of 1.0% differ by a factor of 10, with the film grown without H_2 dilution having the higher conductivity and lower activation energy. This is consistent with the fact that hydrogen atoms can, under certain circumstances combine with dopant atoms to produce local bonding configurations that reduce the doping efficiency of the B- and P-atoms.

4. SUMMARY

We have deposited undoped a-Si,C:H and µc-Si,C:H by RPECVD. In addition we have been able to dope these films p-type and n-type by the downstream addition of the respective doping gases, PH_3 and B_2H_6. Our studies show that the electrical and optical properties of the alloy RPECVD films are similar to those of films deposited by the conventional GD process. In addition our results establish that for the µc-Si,C:H alloys, the crystalline component is Si, and the amorphous component is a-Si,C:H. There is no spectroscopic evidence for the incorporation of the C-atoms of µc-Si,C:H into any other possible crystalline phase, as for example SiC, or graphitic or diamond-structured C. The dark conductivities of the most heavily doped p-type and n-type µc-Si,C:H alloys are orders of magnitude less than those of similarly doped µc-Si, and the dark conductivities of the most heavily doped a-Si,C:H alloys are also orders of magnitude less than those of similarly doped a-Si:H. For the X = 0.67 gas ratio, the dark conductivity activation energies in both the n-type and p-type µc-Si,C:H and a-Si,C:H, are larger than those of the corresponding n-type and p-type µc-Si:H and a-Si:H by about the same energy difference of ~0.2 eV. This aspect of the conductivity data is discussed in some detail in Ref. 7, and is a manifestation of comparable increases in the valence and conduction band offsets between the Si crystallites and the a-Si,C:H component of the µc-Si,C:H alloys, as the C-content increases.

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