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Physical and tribological properties of a-Si_{1-x}C_x:H coatings prepared by r.f. plasma-assisted chemical vapour deposition

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a-Si_{1-x}C_x:H films deposited by r.f. plasma-assisted chemical vapour deposition were studied as a function of their composition. The friction and wear properties were investigated with the help of a conventional ball-on-disc apparatus. These results are correlated with chemical (Si/C atomic ratio) and structural (Raman and infrared spectroscopy) properties. The friction coefficient in a humid ambient atmosphere changes markedly with the carbon fraction and reaches a value as low as 0.05 for coatings with 70 to 90 at.% C. The carbon-rich films consist of diamond-like carbon with silicon.

1. Introduction

Amorphous hydrogenated silicon carbide (a-Si_{1-x}C_x:H) films have received considerable interest over the last years due to their promising applications as a variable bandgap material in thin film technology. Remarkable improvements have been obtained in the cell performance of amorphous silicon solar cells employing a-SiC:H as a wide-gap window layer (1). Recently, Oguri and Arai (2) reported on the excellent mechanical (tribological) properties of a-Si_{1-x}C_x:H films grown by dc glow discharge at 550°C. They demonstrated that by adding 10-30 at.% Si to a diamond-like carbon (DLC or a-C:H) film, a very low friction coefficient of 0.05 nearly independent of relative humidity (RH) was obtained. This is in contrast to DLC coatings, where it is well known that the friction coefficient depends strongly on the ambient relative humidity. The friction coefficient increases from about 0.05 in a dry nitrogen (N₂) atmosphere or under UHV conditions, to a value between 0.2 and 0.3 above about 10% RH (3).

In this paper, we report on the physical and tribological properties of a-Si_{1-x}C_x:H films grown by r.f. plasma-assisted chemical vapour deposition (PACVD) at low temperatures (below 300°C).

2. Experimental details

a-Si_{1-x}C_x:H films were deposited in a capacitively coupled r.f. parallel-plate PACVD reactor (electrode diameter: 20 cm) from silane (SiH₄) and methane (CH₄) mixtures. The total gas flow rate was fixed at 10 sccm, the pressure at 1.5 Pa and the r.f. power at 100 W. The CH₄ to SiH₄ gas flow ratio was varied to prepare films of various

compositions (x ranging from 0 to 1). Films were deposited on the powered electrode. The negative dc self-bias voltage on this electrode was around 400 V throughout this study. The ion bombardment raises the substrate temperature up to $220 \pm 50^\circ\text{C}$. AISI 304 stainless steel, polished silicon and Corning 7059 glass were used as substrates.

The silicon content of the $a\text{-Si}_{1-x}\text{C}_x\text{H}$ films was determined using electron probe micro-analysis (EPMA) on $2 \mu\text{m}$ films grown on the stainless steel substrates. The samples were conductively coated with Al to remove errors caused by charging. The SiK_α -signal intensity of the specimens was compared with a crystalline silicon reference. The carbon content was then calculated assuming that the films consist solely of carbon and silicon, thus neglecting the presence of hydrogen. The results were verified with Rutherford Back Scattering (RBS) measurements, which yielded consistent values within 10% of the EPMA results.

Optical absorption coefficients and refractive indices were determined from transmission measurements in the $0.4\text{--}2 \mu\text{m}$ wavelength range on the coated glass specimens. For the determination of the optical gap, we avoided the use of the conventional Tauc plot which requires an extrapolation subject to relatively large errors. Instead, we have used the energy ($E_{0.1}$) at which the absorption coefficient equals 10^4 cm^{-1} , as an indication of the optical gap. The refractive index was calculated from the interference fringes in the region of weak absorption ($\lambda > 1 \mu\text{m}$) using the method described by Swanepoel (4).

The structure of the films was determined by IR spectroscopy, Raman scattering and X-ray diffraction (XRD). IR transmission measurements ($400\text{--}4000 \text{ cm}^{-1}$ range) were performed on $1.5 \mu\text{m}$ thick films deposited on double-polished Si substrates. The IR spectra were recorded using an uncoated silicon wafer as reference. It was necessary to use a baseline correction in order to obtain a zero level background for each absorption peak. Due to the nearly complete lack of baseline resolution in the $400\text{--}1100 \text{ cm}^{-1}$ region, it was impossible to compensate completely for the interference fringes in this spectral region. Therefore, the resulting bands in this region can only be analyzed qualitatively. Raman spectra were measured at room temperature in backscattering geometry with the 514.5 nm line of an Ar ion laser.

The friction and wear properties were investigated with the help of a conventional ball-on-disk apparatus. The friction coefficients were obtained by unlubricated sliding of a virgin steel ball (AISI L3; diam: 6.35 mm) on the stainless steel-coated disks with a normal force of 1, 5 and 10 N . The disks rotated at 500 rpm and the sliding radius varied between 2 and 8 mm . The humidity of the N_2 atmosphere within the test chamber could be controlled between 0 and 100% RH. The friction coefficient was determined in a dry N_2 and in a wet N_2 (RH=50%) test atmosphere. On each sample, up to four tests were performed with a maximum duration of 24 hours.

3. Results and discussion

3.1 Chemical composition

The methane volume fraction $X(\text{CH}_4)$ ($=Q(\text{CH}_4)/(Q(\text{CH}_4)+Q(\text{SiH}_4))$, where Q represents the gas flow rate) was varied in order to study its influence on the coating composition. Figure 1 shows the carbon content in the film as a function of $X(\text{CH}_4)$ as determined by EPMA. The carbon content in the film increases proportionally with increasing methane volume fraction. The carbon content in the film is always slightly lower than expected from the gas phase composition. However, it is possible to obtain high carbon concentrations in the films. This suggests that our films are grown in the "high-power" regime (5). In this regime, both silane and methane are efficiently decomposed by the

plasma. In the "low-power" regime, methane is hardly decomposed by the plasma. In this case, the amount of carbon that can be incorporated in the film is limited to less than 40 at.%, whereas in the high power regime alloys with arbitrary Si/C proportions can be grown depending on the deposition conditions. Such behaviour is not surprising owing to the different activation energies of SiH_4 and CH_4 in a glow discharge (6).

3.2 Optical properties

Figure 2 shows $E_{0.4}$ and the refractive index n as a function of the carbon fraction in the film. It can be seen that as the silicon content increases, $E_{0.4}$ increases up to a maximum at $x=0.6$. The refractive index is nearly constant in this region. A further increase in silicon content leads to a decrease in $E_{0.4}$ towards a value close to that obtained for a-Si:H. A similar trend has been reported by other authors (7,8).

Figure 1 Carbon content versus methane volume fraction $X(\text{CH}_4)$: $\circ$, EPMA results and ∇ , RBS results.

Figure 2 $E_{0.4}$ (energy at which the absorption coefficient is 10^4 cm^{-1}) and the refractive index n as a function of the carbon fraction in the film.

3.3 Structural characterization

3.3.1 IR measurements

Film structure was mainly studied using IR absorption spectroscopy. This technique is now generally accepted to be one of the most elegant techniques for the structural evaluation of amorphous materials. The IR spectra of our films have the same structure as the spectra reported by Wieder et al. (9). They can be divided into four regions characterized by distinct vibrational modes: CH_n stretching ($2800\text{--}3200\text{ cm}^{-1}$), SiH_n stretching ($1900\text{--}2300\text{ cm}^{-1}$), bending of CH_n groups attached to C or Si, CH_n bending and deformation and C-C stretching ($1100\text{--}1700\text{ cm}^{-1}$) and overlapping stretching, rocking, wagging and bending modes of (CH_n) groups attached to C or Si, SiH_n and SiC ($500\text{--}1100\text{ cm}^{-1}$).

Figure 3 Evolution of the C-H stretching absorption band (a) and the Si-C absorption band (b) with the composition of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ films.

Figure 3a shows the evolution of the C-H stretching mode around 3000 cm^{-1} as a function of x . For $x < 0.6$ the absorption band was too weak to obtain any useful information on the bonding state of the carbon atoms. A tentative assignment of the peaks contributing to this broad absorption band can be found in (10). It can be clearly seen that with increasing silicon content the peak maximum shifts from 2930 cm^{-1} to 2870 cm^{-1} . Furthermore, the absorption intensity at the higher wavenumber side of the peak ($3000\text{--}3200\text{ cm}^{-1}$) drops continuously. The decrease of the absorption around 3000 cm^{-1} which can be attributed to sp^2 CH modes, indicates that silicon promotes the formation of sp^3 carbon sites in the film. This can be easily understood since Si can only have sp^3 -hybridization. Together with this decrease in absorption around 3000 cm^{-1} , we observed a decrease in absorption around 1600 cm^{-1} (sp^2 C-C stretching vibrations). A similar change from threefold to fourfold coordination of the carbon atoms with increasing silicon content has been measured by NMR by Yamamoto et al. (11). As the C-H stretching absorption modes are not markedly affected as regards peak position by the alloying with silicon atoms (12), the peak shift with increasing silicon fraction has to be attributed to a change in the absorption strength of the different modes. We believe that this frequency shift is due to an increase of the fraction of sp^3 CH_3 bonding sites in the film relatively to the sp^3 CH_2 (and CH) bonding

sites. Together with this peak shift, we see an increase in the number of H atoms attached to carbon. The concentration of the CH_3 groups, however, is still low since the absorption from the methyl group symmetric deformation mode around 1250 cm^{-1} is small (around 100 cm^{-1}). Rynders et al. (13) reported values up to 1000 cm^{-1} for this absorption mode for a-SiC:H films grown from tetramethylsilane where most of the carbon atoms were incorporated in chain terminating methyl groups. Nevertheless, one should be aware that this analysis can not give a complete picture of the carbon surrounding since we only observe protonated carbon atoms. The absorption modes between 1100 and 1700 cm^{-1} are another source of information concerning the bonding environment around incorporated carbon atoms. Unfortunately, most vibrational modes in this region are very weak and are thus of limited utility.

Figure 3b shows the evolution of the absorption region around 800 cm^{-1} as a function of carbon content in the film. With increasing carbon content, the peak around 780 cm^{-1} grows up to $x=0.61$. Using the assignment proposed by Mohr et al. (14), the increased intensity of the peak around 780 cm^{-1} and the shift of the peak to higher wavenumbers indicate an increase in the amount of Si-C bonding or amorphous silicon carbide structure in the film with increasing carbon content. The decrease of intensity with higher carbon content is due to a decrease in the degree of heteronuclear Si-C bonds. The broad band around 1000 cm^{-1} is difficult to assign due to the overlapping of a number of bands.

Figure 4 Evolution of the Raman spectra with the composition of $\text{a-Si}_{1-x}\text{C}_x\text{:H}$ films: (a) spectra for the carbon-rich films; (b) spectra for the silicon-rich films.

3.3.2 Raman measurements

To support our IR measurements, we performed Raman measurements. Figure 4 shows the Raman spectra of the different films. The broad Raman peak around 1550 cm^{-1} (the so-called G-peak) with a shoulder at 1400 cm^{-1} (the so-called D-peak) for $x=1$ is characteristic for hard DLC films. It is generally accepted that this Raman peak is due to scattering from π -bonded sp^2 carbon clusters (15). The shift of these bands towards lower wavenumbers with increasing Si content is partly due to the coupling of the lighter carbon atoms to the heavier silicon atoms (16). The D-peak decreases in intensity relatively to the G-

peak with increasing silicon content. Tamor et al. (17) showed that the G-peak shifts to lower wavenumber and the I_D/I_G intensity ratio decreases with smaller cluster size. This suggests that the size of the carbon clusters in our films is decreasing with increasing silicon content. Thus, the sp^3 concentration is increasing relatively to the sp^2 concentration.

For the silicon-rich films, we can see a small scattering around 480 cm^{-1} , which corresponds to the TO phonon mode in amorphous silicon. The Raman scattering at around 520 cm^{-1} is due to the crystalline silicon substrate. Raman signals associated with Si-C bonds have not been clearly identified. The Raman spectra clearly indicate the formation of homonuclear carbon and silicon bonds in the carbon-rich and silicon-rich $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films.

3.3.3. Film structure

X-ray diffraction measurements indicate that the films are amorphous over the whole investigated composition range. The amorphous character of our films is not surprisingly since the substrate temperature is too low to produce any crystallization within the deposited SiC layer. Our infrared and Raman measurements clearly support the structural model of $a\text{-SiC:H}$ which has recently been proposed by Robertson (18). In Si-rich alloys, Si-Si bonds form a network (as seen in Raman measurements) and with increasing carbon fraction in the film, Si atoms are progressively replaced by C and CH_n groups. With increasing x , the SiC-alloy becomes chemically ordered (increase in the 780 cm^{-1} IR band). As a consequence of this ordering, the bandgap increases. For $x > 0.5$, the bandgap opens up more rapidly as Si-C bonds are replaced by the even stronger C-C bonds. The small rise in E_{04} for $x < 0.4$ suggests that our films have only a moderate chemical ordering. Above $x = 0.6$, the presence of C-C bonding and C=C sp^2 sites becomes more and more important (Raman and IR). sp^2 C atoms will segregate into π -bonded clusters and these clusters will control the bandgap. As the optical gap of compact aromatic clusters is inverse proportional with the number of rings in the clusters (19), the bandgap will decrease with increasing carbon fraction, since the Raman spectra indicate an increase in cluster size. With increasing silicon content, the film structure is changing from a cross-linked diamond-like carbon material to an amorphous silicon carbide material with a polymer-like structure.

Figure 5 Friction coefficient in dry (a) and wet N_2 (b) as a function of the carbon fraction x in the film for normal loads of 1, 5 and 10 N.

3.4 Friction behaviour

The friction coefficients of our $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films in dry and wet N_2 (50% RH) for normal loads of 1, 5 and 10 N are shown in figure 5. Under dry N_2 conditions, the friction coefficient is independent of the carbon fraction in the film ($x \geq 0.7$). In humid N_2 atmosphere, a minimum friction coefficient between 0.05 and 0.1 is achieved for a silicon content between 10 and 30 at.%. The values shown in the figure are minimum steady-state friction coefficients $\mu_{\text{min,ss}}$, defined as the minimum friction coefficient that lasted during a sufficiently long sliding period (about 1 hour). For $x < 0.7$ under dry conditions and for $x < 0.6$ in humid N_2 atmosphere, these minimum steady-state friction coefficients could not be determined because the load bearing capacity of these films was too low. From our Raman measurements, it is clear that this load bearing capacity is closely connected with the diamond-like carbon character of the material. The low friction coefficient for $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ with x between 0.7 and 0.9 cannot be explained entirely by the diamond-like carbon structure. For both type of films, the wear mechanism consists in material transfer from the coating to the counterbody in the tribological system (20). In the case of DLC, this transfer layer is reported to be a graphite or hydrocarbon-rich film (3, 21). In the case of $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ ($x = 0.7$ to 0.9), it consists of graphite-like carbon including hydrogen under dry conditions and of a hydrated silica in a humid atmosphere, which would account for the very low friction coefficient (22). More detailed results of the mechanical characterization and the wear properties of these films as a function of normal load and relative humidity will be published elsewhere (23).

4. Conclusions

$a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films with carbon fraction varying from 0 to 1 were prepared by means of r.f. plasma decomposition of CH_4 and SiH_4 at substrate temperatures below 250°C . The optical properties exhibit a strong dependence on the carbon content in the film. Raman and IR spectroscopy show that carbon-rich $a\text{-Si}_{1-x}\text{C}_x\text{:H}$ films have a diamond-like carbon structure. With increasing silicon content, films with an amorphous silicon carbide structure are obtained. The degree of chemical ordering is maximum around the stoichiometric composition. Ball-on-disc measurements show a strong composition dependence of the friction behaviour of these films. For coatings with 70 to 90 at.%, C, friction coefficients as low as 0.05 are obtained in humid ambient atmosphere.

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