# AMORPHOUS CARBON-SILICON ALLOYS PREPARED BY A HIGH PLASMA DENSITY SOURCE

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## ABSTRACT

The addition of silicon to hydrogenated amorphous carbon can have the advantageous effect of lowering the compressive stress, improving the thermal stability of its hydrogen and maintaining a low friction coefficient up to high humidity. Most experiments to date have been on a-$C_{1-x}Si_x$:H alloys deposited by RF plasma enhanced chemical vapour deposition (PECVD). This method gives alloys with considerable hydrogen content and only moderate hardness. Here, we use a high plasma density source, the electron cyclotron wave resonance (ECWR) source, to prepare films with a high deposition rate. The composition and bonding in the alloys is determined by XPS, visible and UV Raman and FTIR spectroscopy. We find that it is possible to produce hard, low stress, low friction, almost humidity insensitive a-$C_{1-x}Si_x$:H alloys with a good optical transparency and a band gap over 2 eV.

## INTRODUCTION

Amorphous C-Si (a-$C_{1-x}Si_x$) and hydrogenated amorphous C-Si (a-$C_{1-x}Si_x$:H) alloys are of both fundamental and technological interest. The fundamental interest arises from the possibility of studying the preference for chemical ordering or heteroatom bonding in a tetrahedrally coordinated $sp^3$ bonded alloy system around x=0.5, where the crystalline compounds exists. The technological interest arises from the possibility of obtaining low stress, low friction, humidity insensitive coatings [1-3]. Moreover band calculations suggest that the band gap of C-rich alloys depends on the C-C bonding, not the C-Si bonding, so that band gap need not be reduced by the addition of silicon [1]. It should thus be possible to produce hard, low stress, low friction, almost moisture insensitive a-$C_{1-x}Si_x$:H alloys with a good optical transparency and a band gap over 2 eV.

Most of the studies conducted so far considered the introduction of Si into hydrogenated amorphous carbon (a-C:H) produced by PECVD or Electron Cyclotron Resonance, see ref. [4] for a review. Hydrogenated tetrahedral amorphous carbon (ta-C:H) can be deposited using a Plasma Beam Source [5] or an Electron Cyclotron Wave Resonance Source [6]. In a-C:H a high $sp^3$ content is obtained mainly by saturating C=C bonds as $CH_x$ groups rather than by increasing the fraction of C-C bonds. Ta-C:H differs in that a higher $sp^3$ content occurs at a fixed lower H content of 25-30%. This results in ta-C:H having a higher density (up to 2.4 g/cm$^3$ [7]), Young's modulus (~300GPa [8]) and hardness [5] and a lower H content, compared to a-C:H with similar $sp^3$ content. On the other hand, the higher ion energy and ionisation obtained in the ECWR source, with respect to PECVD, results in much higher stresses of ~6-7 GPa [6], similar to as-deposited ta-C, limiting the maximum achievable thickness to ~100nm. This contrasts with as-deposited diamond like a-C:H which has ~1-2 GPa of stress.

The friction coefficient, $\mu$, of a-C:H is very low (0.03-0.05) in inert atmosphere in low humidity conditions, but rises to ~0.5 at high humidity [9], whilst diamond is humidity insensitive. On the other hand laser-deposited ta-C has a higher value of ~0.2 at low humidity, decreasing slowly with increasing humidity [10]. Gangopadhyay et al.[11] and Oguri et al.[2,3] have shown that Si introduction in a-C:H could reduce 50%-80% the stress and result in friction coefficients lower than 0.1 up to 80% humidity. However, for a fixed bias voltage, only a ~37% stress reduction was achieved [11]. In this paper the effect of Si introduction on the structure and properties of ta-C:H is presented.

## EXPERIMENT

### Deposition

Films were deposited using an ECWR source (Fig 1) at room temperature from a $SiH_4/C_2H_2$ mixture, with gas ratio R= $SiH_4$ (sccm)/[$C_2H_2$(sccm)+$SiH_4$(sccm)] varying from 0 to 100%, to produce all a-$C_x$:$Si_{1-x}$:H alloys from ta-C:H to a-Si:H. The ECWR, or WAve Resonance Plasma source (WARP), is a 13.6 MHz single turn inductively coupled source. A grounded extraction electrode completes the assembly (Fig 1). The transverse magnetic field generated via the Helmholtz coils splits the electromagnetic waves in two circularly polarised waves. The right hand polarised wave is no longer reflected by the plasma, but is strongly coupled to the bulk plasma, so allowing efficient power transfer from the RF to the plasma, and enabling the formation of a high plasma density up to two orders of magnitude higher than in a capacitive source. The wave resonance condition is achieved when a stanting wave is set up within the source cross section [6]. In each case the deposition conditions were fixed, with the exception of R. The operating pressure was ~$1.2x10^{-3}$ mbar, maintained by a turbomolecular pump, with a pumping speed of 1600 l/s. The RF power was 285W, the voltage and current across the Helmholtz coils were ~4.71V and ~980mA, respectively, resulting in an ion energy of ~150eV for a 100% $C_2H_2$ plasma [6].

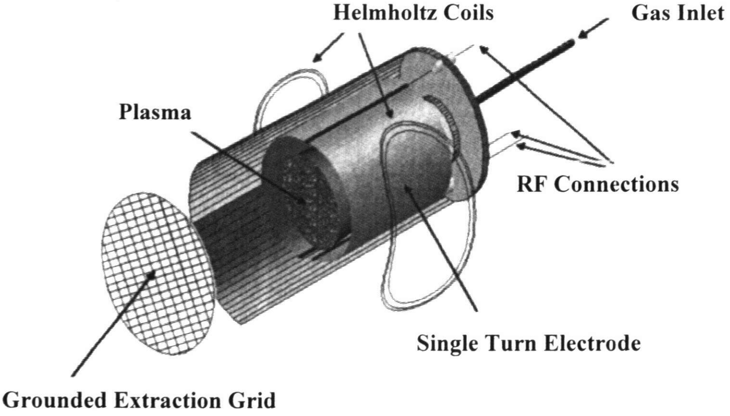

Fig 1. Schematic diagram of the ECWR source

## Characterisation

Films were deposited on Si and quartz for structural, mechanical and optical characterisation. Film thickness and refractive index at 633nm were determined by Ellipsometry (Gaertner Scientific L117). Film stress was determined using Stoney's equation. The surface curvature of the Si substrate, before and after deposition, was measured by a Sloan DektakIIa profilometer. The optical gap ($E_{04}$ and Tauc) and complex refractive index were measured with an Ati-UNICAM UV-visible spectrometer. Visible Raman spectra (at 514.5nm) were collected in a Renishaw micro-Raman 2000 spectrometer. UV-Raman spectra (at 244nm) were collected on a UV-enhanced CCD camera on a Renishaw micro-Raman system 1000, modified for use at 244nm, with fused silica optics throughput. Fourier Transform Infra-Red spectrometry (FTIR) was performed on a ATI-Mattenson RS1 system. The C/Si ratio in the films was investigated by X-Ray Photoelectron Spectroscopy. The percentage of $sp^3$ bonded carbon content was derived analysing the carbon K edge in the High loss Electron Energy Loss Spectra (EELS). EELS measurements were carried out on a dedicated VG501 scanning transmission electron microscope fitted with a spectrometer with a McMullan parallel EELS detection system [7]. Friction measurements were performed on a ball-on-disk tribometer. Stainless steel balls (AISI 52100, 6.35 mm diameter) were used during tests, which were conducted both in air and under a controlled humidity environment (10, 50 and 80% relative humidity). A load of 2N was applied, corresponding to a Hertzian contact pressure of 370 MPa. A sliding speed of 0.3m/s was used in each of the measurements. A second series of friction measurements were performed with DLC-coated steel balls. An a-C:H layer was deposited with a PECVD system, at 200 W and 100mTorr pressure. In this conditions a typical diamond-like a-C:H is obtained on Si, with a Tauc gap of ~1.5eV.

## RESULTS

The deposition rate was 7.5-5 Å/s, slightly decreasing with increasing relative silane flow rate R. This is comparable with the deposition rate reported by Oguri et al. [2,3] and Gangopadhyay et al.[11], but 5 to 10 times higher than ECR deposited films [12]. Fig 2 shows the stress as a function of R. A stress reduction of ~45% is observed for R=10% , similar to what reported by Gangopadhyay [11] for films grown at a fixed bias voltage. Almost full stress release happens only for R>60%. However films thicker than 500nm could be grown at R=20%. The refractive index at 633Å remains ~2.2 until R~60%, then increases towards ~3.2, typical of a-Si:H. Fig 3 displays the optical gap ($E_{04}$ and $E_{Tauc}$) as a function of R. $E_{04}$ starts at ~2.1 eV, typical of ta-C:H, increasing to a maximum of ~3.2 eV for R=70/80%, before decreasing towards values typical for a-Si:H. This suggest that R=70/80% corresponds to C/Si ~40-50% within the films thus indicating a lower Si incorporation than R. This is consistent with XPS data, Fig 4(Si/[C+Si]=42% at R=80%).

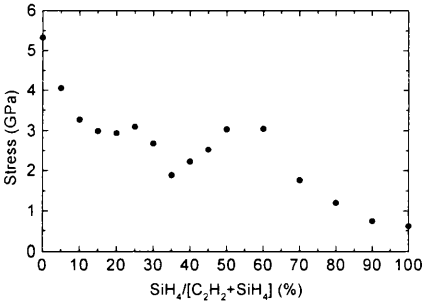

Fig 2: Stress vs. R

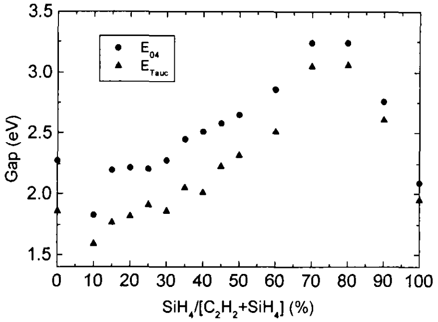

Fig 3: Optical gap vs. gas flow ratio R

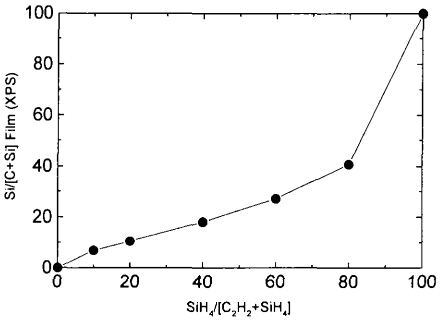

Fig 4: Si/[C+Si] ratio in the films vs. R

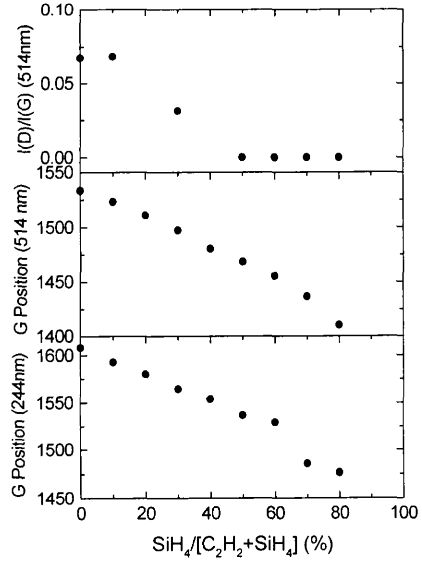

Fig. 5 Variation of I(D)/I(G) and G position in 514nm Raman and G position in UV Raman vs. R

Fig 5 shows G peak position and the ratio of intensities of D peak and G peak, I(D)/I(G), for 514nm Raman and G peak position for UV Raman. The G peak is due to the relative motion of $sp^2$ carbon atoms, whilst the D peak is due to breathing modes of aromatic clusters [13]. The as-deposited ta-C:H still shows a very small D peak, but increasing Si content opens up the remaining rings, resulting in a olefinic $sp^2$ structure and a higher optical gap [1]. This is reflected in the decrease of the ratio I(D)/I(G). The decrease in G peak position both in visible and in UV Raman is explained by the softening of the C=C modes induced by the increasing number of softer C-Si bonds, due to the heavier Si mass. The absence of any C $sp^2$ ring clustering is further shown by the parallel behaviour of the G peak in UV Raman and Visible Raman, the latter being just downshifted by ~72cm$^{-1}$ with respect to UV. This means that there is an unique C $sp^2$ configuration corresponding to a given Si content, thus allowing a direct quantification of the Si/C ratio from Raman parameters (cfr. Fig 4/5) [14]. Thus we can assert that the fraction of C-C $sp^3$ does not decrease with Si addition [13]. This is confirmed by EELS measurements, that give an almost constant $sp^3$ fraction ~70% up to R=40%. The evolution of the bonding structure has been also investigated by FTIR, shown in Fig 6,7 for R=0,20,40,60,80,100 %. Fig 6 shows the increasing contribution of the C-Si stretching band at ~770cm$^{-1}$ [12], with increasing R. It reaches a maximum for R=80%, then being replaced by the Si-$H_n$ modes of a-Si:H (R=100%) [12]. Fig 7 shows an increase of the Si-$H_2$ stretching modes at ~2100 cm$^{-1}$ relative to the C-$H_x$ stretching at 2800-3100 cm$^{-1}$. Note also the progressive disappearance of the high frequency C-$H_x$ $sp^2$ modes [12,15] with increasing R. In particular, at R=80% there is

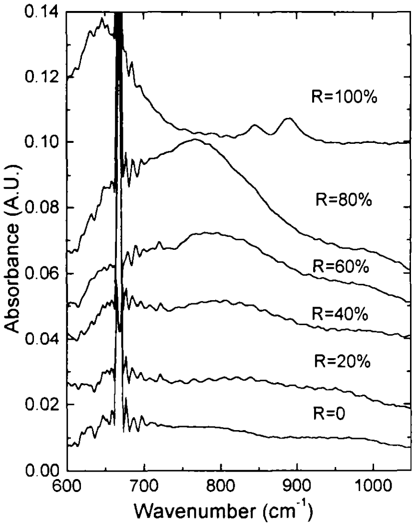

Fig 6: low frequency FTIR spectra of some samples with increasing R

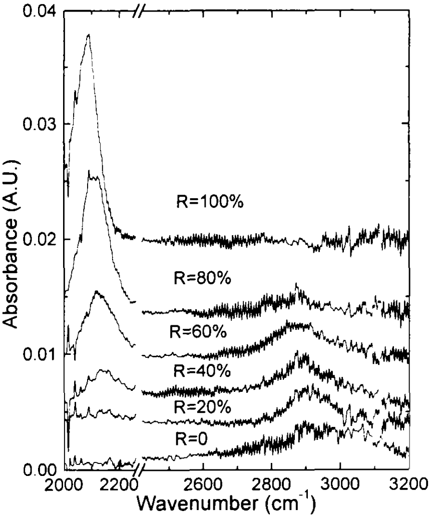

Fig 7: high frequency FTIR spectra of some samples with increasing R

a maximum at 2870 cm$^{-1}$ corresponding to sp$^3$ $CH_3$ symmetrical stretching vibrations [12,15], with a lower frequency shoulder due to sp$^3$ $CH_2$ symmetrical stretching [12,15]. This again confirms that samples at R=80% have the highest Si-C bonding, resulting in the highest C sp$^3$ fraction and optical gap. A similar trend in the Si-C and Si-H vibrations is seen in UV Raman data.

The Young's Modulus of an as-deposited ta-C:H is ~300 GPa, as measured by Brillouin Scattering [8], with Poisson's Ratio of ~0.3. Nanoindentation was performed on thick (>500nm) samples grown at R=20% and 40%, resulting in hardness of at least 15 GPa for R=40%.

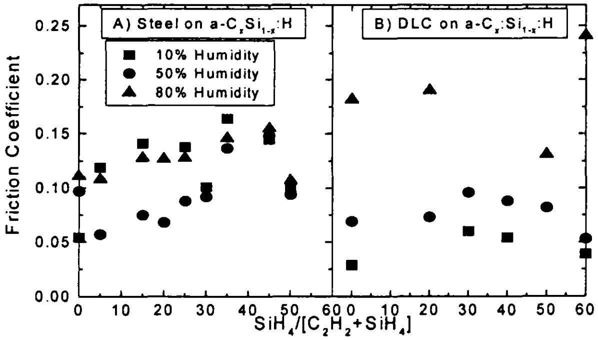

Fig 8. Friction coefficient at 10, 50 80% humidity for a-$C_x$:$Si_{1-x}$:H films vs. R for A) steel ball, B) diamond-like a-C:H coated steel ball

Friction tests were conducted for 2 hours. Fig 8 shows the steady friction coefficients. As-deposited ta-C:H, without Si, shows excellent friction properties in the range 10-80% humidity ($\mu$=0.05-0.12). This is comparable with Si incorporated a-C:H [2,3], whilst $\mu$ for a-C:H is known to increase with humidity up to 0.5 [9]. For

R>50%, with steel balls, and R> 60%, with DLC coated balls, film failure was observed with μ~0.6. Increasing R gives a slight increase in μ, but always less than ~0.15. Furthermore, high and low humidity result in roughly the same μ, with a minimum at 50% humidity. Thus Si addition is useful to obtain low stress, low humidity sensitive films. Sliding against a DLC coated ball gives a very low μ at 10% humidity (~0.02-0.05). However, in this case, there is a sensible increase in μ with humidity, due to the deterioration of the friction properties of a-C:H coating the ball.

## CONCLUSIONS

We have demonstrated that the ECWR source can be used for high rate deposition of a-$C_x$:$Si_{1-x}$:H alloys, ranging from ta-C:H to a-Si:H. We have analysed the structural and optical properties of these alloys. Ta-C:H shows a low, almost humidity insensitive friction coefficient of ~0.05-0.1. Si introduction (~10% Si/[C+Si]) allows a ~45% reduction of the stress, whilst maintaining low friction and low humidity sensitivity. Coatings with high hardness, low stress, low friction, and an optical gap of 2.5 eV can thus be deposited, satisfying the requirements for a wide range of possible applications.

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