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A Comparative Study of Iron-Based Film Deposition from Iron Pentacarbonyl at 248 nm and 488 nm

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Abstract. Thin film deposition by laser irradiation of $\text{Fe}(\text{CO})_5$ at two radiation wavelengths (248 nm and 488 nm) was performed. A perpendicular geometry of irradiation was used. Maximum deposition rates of 14 Å/s at $\lambda = 248$ nm and 1.5 Å/s at $\lambda = 488$ nm were obtained, indicating a diffusion limited process. SEM analysis of film morphologies showed significant differences in the nucleation and growth of films deposited at 248 nm and 488 nm. XPS surface analysis revealed a higher carbon content and carbide phases in the surface of films deposited at 488 nm on SiO_2 (quartz) substrates. Oxidized surface Fe phases were found in films, with increasing the exposure time to laser radiation. The film properties are discussed in connection with irradiation conditions and specific mechanisms involved.

1. INTRODUCTION

The laser photochemistry of transition metal carbonyls continues to be of a major interest, due to the localised deposition of refractory metals which is of potential utility in microelectronics and electro-optics. The purity of laser-deposited films depends in a critical way on the kinetics developing in vapour and/or adsorbed phases during laser irradiation and on the interaction of photo-fragments with the substrate surface [1].

The laser assisted CVD from metal carbonyls may be driven at different wavelengths and irradiation regimes, with specific features according to the prevailing photolytic [2,3] or pyrolytic [4] process involved. In particular, deposition of iron from $\text{Fe}(\text{CO})_5$ was obtained by UV laser excitation [5,6] and by laser-induced thermal decomposition, either at a heated surface [4] or in sensitized gas-phase reactions [7]. Studies relevant to the metal photodeposition revealed that the carbonyl decomposes into coordinatively unsaturated species and carbon monoxide by UV and visible light excitation to electronically excited states. At the same time, the thermal and photochemical processes developing at surface under laser radiation are introducing new channels for the dissociation of fragments and for the desorption of molecular CO [5,7].

In the present work we have carried out a series of depositions from $\text{Fe}(\text{CO})_5$, by employing the UV (at 248 nm) and the visible (at 488 nm) laser radiation.

A comparative study of the growth dynamics, chemical content and morphology of films was performed in connection with experimental conditions and irradiation regimes. An investigation of changes induced in film composition by the nature of the substrate is also presented.

2. EXPERIMENTAL

The irradiation of $\text{Fe}(\text{CO})_5$ was conducted at room temperature, in the static mode. The deposition cell was precleaned in a standard vacuum line provided with on-line liquid nitrogen traps. Before filling the cell, the $\text{Fe}(\text{CO})_5$ was purified by freeze - pump - thaw cycles.

During all processing experiments, the carbonyl pressure was maintained at 5 torr. This pressure value was chosen in order to model practical conditions for film deposition. A KrF laser (pulse length ~ 10 ns, repetition frequencies ~ 1 Hz, pulse energy ~ 30 mJ) and a CW Ar⁺ laser (output power 60 mW) were used alternatively in a perpendicular configuration relatively to the SiO₂ (fused silica) substrate. In some Ar⁺ laser experiments, polycrystalline silicon wafers were also used as substrates. The excimer laser beam was focused at a distance of about 1 cm behind the cell front window, on which the deposition occurred. The dynamics of film growth was investigated at increased number of pulses (15, 20, 30, 50, 75, 100, 300 and 500 laser pulses). In the Ar⁺ laser experiments, the radiation was focused onto the substrate (power density 10^2 W/cm²) which was positioned 6 cm behind the entrance window (about 1% radiation attenuation at 5 torr Fe(CO)₅ pressure). The deposition was carried out at different irradiation time periods (running from 1 to 22 minutes).

The thickness of the deposited films was measured by interference microscopy (MIT - 4 LOMO microscope).

The chemical composition of the films was analysed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MK II spectrometer (base pressure $\sim 9 \times 10^{-10}$ mbar). For XPS, AlK α radiation ($h\nu = 1486.6$ eV) was employed. The calibration of spectra was performed by means of the Ag 3d_{5/2} ($E_B = 368.26$ eV) line, with the Fermi level as an energy reference. A "flood gun", was used for the correction of charging effects while the position of the Si2p level in SiO₂ (at 103.4 eV) and in Si (at 99.7 eV) was taken as a reference for depositions on quartz and silicon substrates, respectively.

3. RESULTS AND DISCUSSIONS

The variation in film thickness (d) with increasing number (N) of UV pulses and irradiation time (t) is displayed in Fig.1 (a) and Fig.1 (b), for films grown at 248 nm and 488 nm, respectively.

Figure 1: a. - The dependence of film thickness d (squares) and of d^2 (circles) on number of pulses (KrF laser); b. - The dependence of film thickness d (triangles) and of d^2 (circles) on exposure time (CW Ar⁺ laser) in case of SiO₂ (curves 1) and Si (curves 2) substrates

One may observe that the UV radiation is much more effective in inducing Fe(CO)₅ decomposition and subsequent film growth than the 488 nm radiation. Using SiO₂ substrates, a film thickness of more than 1000 Å could be reached in less than $N = 300$ pulses (about $3 \cdot 10^3$ ns effective irradiation time). The

UV deposition rate varied from 14 Å/pulse to 0.7 Å /pulse as increasing the number of pulses from $N = 20$ to 500 pulses, respectively.

Depending on the substrate used in the deposition process (either quartz or silicon) the interaction of the Ar^+ laser radiation with iron carbonyl was leading to films with different thicknesses for the same irradiation time (curve 1 for SiO_2 and curve 2 for Si substrates, respectively, Fig. 1(b)). The deposition rates were running from 1.5 Å/s (SiO_2 substrate) to much lower values (about 0.8 Å /s) when Si substrates were used . In both cases a marked decrease in deposition rate was recorded for long exposure times (less than 0.1 Å /s for $t = 20$ min). The low deposition rate for films deposited on Si substrates may be explained if we consider that in primary stages of film growth nucleation sites are formed by direct decomposition of adsorbed species [8]. In case of carbonyls , investigations of their molecular adsorption properties on silicon surfaces over a wide range of temperatures [9] have shown that carbonyls desorb almost completely at substrate temperatures well below room temperature (around 250 K).

The linear dependence of d^2 with irradiation time (dashed lines in Fig. 1(b)) points out a diffusion limited process developing at 488 nm [8]. A similar law seems strictly to apply at low number of pulses (less than $N = 200$ pulses) in case of the UV processes (dashed line in Fig. 1(a)).

a.

b.

Figure 2: Scanning electron micrographs of films obtained at two different regimes of laser irradiation: a - pulsed UV KrF laser (20000 X), 300 laser pulses , SiO_2 substrate; b - CW Ar^+ laser (7000 X), 1 min irradiation time , SiO_2 substrate.

Scanning electron micrographs showed an essential difference in the nucleation and growth of the films deposited at 248 nm and 488 nm (Fig.2). Irregular aggregates of particles with almost spherical shape are observed in UV irradiation (Fig.2(a), for a film grown at $N = 300$ pulses) while at a lower magnification , the films showed surface wave-ripples, usually associated with surface photodissociation processes [3]. The films deposited on quartz substrate by $\text{Fe}(\text{CO})_5$ decomposition in the 488 nm wavelength range exhibited a dendritic film growth (Fig.2(b), for a film obtained after 7 min of irradiation) pointing out a diffusion limited aggregation (DLA) mechanism, in which surface diffusion and cluster - cluster aggregation play the main role.

XPS analysis was performed in order to detect the C and O content and the chemical states of deposited films under different experimental conditions. The data were obtained for samples exposed to the ambient and the results should account for oxygen and carbon contamination and/or subsequent reactions of the film with air.

Figure 3 presents the variation of the Fe/C and Fe/O atomic ratios with exposure time for films deposited at 248 nm on SiO₂ substrates (Fig.3 (a)) and at 488 nm (Fig.3 (b)) on SiO₂ (triangles) and Si (squares) substrates. One may notice a significant amount of surface carbon incorporation in films obtained by CW laser irradiation of Fe(CO)₅, which further increases when SiO₂ substrates are used. The Fe/C and Fe/O ratios increase in UV films, as the number of laser pulses increases.

Figure 3: X-ray photoelectron spectroscopic data for the temporal evolution of surface Fe/C and Fe/O atomic ratios. a - for films obtained by UV irradiation (circles) and b - for films on SiO₂ (triangles) and on Si (squares) substrates, obtained by Ar⁺ laser irradiation

Most of the oxygen content of the films should proceed through a rather abundant contamination: examination of the O1s core level spectra of the deposits and bare surface shows that both are peaking at an almost similar binding energy (BE) value (around 531 eV for chemisorbed oxygen). The O1s line of many of the films exhibited a shoulder (at about 529 eV) assigned in ref. [5] to O in iron oxide.

To elucidate some features of the deposition mechanism the surface chemical states of Fe and C in films were investigated. Figure 4 displays the Fe2p region for samples obtained in different irradiation conditions. The Fe2p_{3/2} component in films obtained at 248 nm with 500 pulses lies at about 710.7 eV and may be associated with high oxidation Fe states [10] while the same component is shifted towards lower BE values (around 708.2 eV) for irradiation at 488 nm (exposure time $t = 10$ min, SiO₂ substrate) and can be attributed to Fe_xC phases [5] (curves 1 and 2 respectively, in Fig.4 (a)). A shift towards higher BE values (at about 709.9 eV) is noticed when deposition at 488 nm on Si substrate was performed (curve 1 in Fig.4 (b), $t = 1$ min).

With the increasing of the exposure time at the Ar⁺ laser radiation, the carbidic forms of Fe in films on SiO₂ substrates are diminishing in favour of oxidized phases (curve 1 at $t = 1$ min and curve 2 at $t = 10$ min, respectively, in Fig. 4(c)). With the increasing of the irradiation time, the deposition on Si substrates exhibits higher Fe_xO oxidation states (curve 3 in Fig. 4 (c), BE peak around 711.5 eV at $t = 8$ min).

The results of an analysis of the C1s core level spectra for films produced with various experimental parameters are summarized in Fig.5. The peak appearing at 283 eV in samples on SiO₂ may be assigned to carbidic carbon [10]. In UV irradiation regime, this peak is slightly shifted towards higher BE values (curve 2 in Fig.5(a), $N = 75$ pulses), attributed in ref. [5] to Fe₃C forms. For the same irradiation time ($t = 5$ min) and wavelength ($\lambda = 488$ nm), the C1s peak has a shift of ~ 1.5 eV towards higher BE values for films

deposited on Si relatively to those on SiO₂ substrates (curves 1 and 2, respectively, in Fig.5(b)). This feature, together with the small shoulder observed at ~ 285 eV, may indicate carbonyl C in different absorption /incorporation states [5]. For deposition on SiO₂, a slight BE shift (of ~ 0.5 eV) is noticed when the irradiation time increases (from $t = 1$ min to $t = 10$ min, curves 1 and 2 respectively, in Fig. 5(c)).

Figure 4: The XPS Fe2p region for surfaces of films deposited in different irradiation conditions: a - KrF laser, $n = 300$ pulses (curve 1) and Ar⁺ laser, $t = 10$ min (curve 2), both on SiO₂ substrates; b - Ar⁺ laser, $t = 2$ min, Si substrate (curve 1) and $t = 1$ min, SiO₂ substrate (curve 2); c - Ar⁺ laser, $t = 1$ min, SiO₂ substrate (curve 1), $t = 10$ min, SiO₂ substrate (curve 2) and $t = 8$ min, Si substrate (curve 3).

The C1s line spectrum for deposition on Si substrate appears at ~ 285 eV (curve 3 in Fig.5(c), $t = 8$ min) which could represent either chemical states of C bound to itself [10] or a higher incorporation of carbonyl groups.

To note that the XPS technique is a surface analysis and that preliminary results on AES depth profile measurements show a much lower carbon content in the bulk of films deposited at 488 nm on Si substrate.

A comparative study of the deposition mechanism consistent with the above mentioned experimental facts should take into account:

- i) the wavelength of the exciting radiation,
- ii) the irradiation regime,
- iii) the nature of the substrate.

In the UV wavelength range the radiation at 248 nm is strongly absorbed by Fe(CO)₅ ($\sigma_{UV} = 2.7 \times 10^{-17}$ cm²) [5] while a much lower cross-section characterizes the carbonyl absorption at 488 nm ($\sigma_{vis} = 4 \times 10^{-19}$ cm²). In these conditions, a photonic channel of Fe(CO)₅ decomposition is driving the UV deposition process (either in the gas phase or at the interface, depending on the particular geometry of irradiation). The bond dissociation energy for the removal of one CO from a gas phase metal carbonyl is lower than the single 248 nm photon energy (~ 4.8 eV).

Figure 5 (a and b): The C1s line spectra for the surface of films deposited under different irradiation conditions: a - Ar⁺ laser, t = 1 min (curve 1) and KrF laser, N = 15 pulses (curve 2), both on SiO₂ substrate; b - Ar⁺ laser, t = 5 min, Si substrate (curve 1) and SiO₂ substrate (curve 2)

Figure 5c: C1s line spectra for the surface of films deposited at 488 nm on SiO₂ (curve 1 - t = 1 min, curve 2 - t = 10 min) and Si (curve 3 - t = 8 min) substrates

The rather low C content in the UV deposited films, as compared to those obtained with the visible CW laser light is due obviously to an efficient photonic/thermal desorption of CO from the already deposited

film [3,5]. The desorption mechanism is enhanced when the number of UV pulses increases. It was shown indeed that gas phase decomposition processes of metal carbonyls are initiating the deposition, while two competing surface channels: photodecarbonylation and thermal decarbonylation further interfere, resulting in lower C and O incorporation [5] (see also the sharp increase of Fe/C and Fe/O atomic ratios, with increasing number of laser pulses in Fig.3(a)).

In the CW Ar⁺ laser interaction with Fe(CO)₅, direct photodissociation of molecules in the gas phase should occur at a much lower rate than in UV irradiation, with consequences on the lowered deposition rate. It is probable that in this case the radiation is acting on a weakly adsorbed molecular layer on SiO₂ substrate, which could provide the necessary pre-nucleation sites. It was shown [11] that even a submonolayer allows photolytic production of an initial distribution of metal nuclei directly on the substrate surface. Further film growth proceeds through addition of carbonyl fragments produced by thermal (pyrolytic) decomposition processes in the gas phase which are favoured by the CW irradiation and the rather high pressure involved. A higher sticking coefficient of atoms on the pre-nucleated region [11] should also contribute to the growth process.

The extremely low absorption cross-section of iron carbonyl at 488 nm, together with the transparency of the SiO₂ substrate in this wavelength region, are both inhibiting efficient photolytic/thermal desorption of carbonyl groups from the growing film, which exhibits carbidic phases (more evident at low exposure time) and high C content (see Figs.3(b), 4(a) and 5(a)).

It was suggested [9] that surface quenching of activated species causes retention of the carbonyl groups and stabilization of activated species. The carbidic and iron oxide forms suppose CO dissociation on surface. Estimated C-O bond energies (4.4 - 4.9 eV in [5]) require a dissociation energy higher than the single-photon energy of the 488 nm laser (~ 2.5 eV). A channel of thermal dissociation should be considered. Although the iron film surface is not equivalent to any specific crystal face, we think that a mechanism similar to that reported in [12] could be active, in which, at low coverage CO dissociation on Fe(100) crystal has an onset temperature of ~ 300 K. Consequently, carbon and oxygen existing in the form of buried CO molecules could undergo slow thermal dissociation at room temperature [5]. This assumption is further sustained by our experimental results showing that Fe/C and Fe/O atomic ratios keep an almost constant value for films deposited at 488 nm with different exposure times.

In contrast, when using an absorbing Si substrate at visible (488 nm) radiation, complementary thermal - induced effects on surface and at the interface may enhance the desorption of CO groups, thus lowering to some extent the carbon incorporation and the formation of carbidic species (see Figs.3(b), 4(b) and 5(b)). However Si substrate heating in initial stages of deposition may have a detrimental effect on the extent of pre-nucleated regions, due to the thermal desorption of Fe(CO)₅ precursor [9]. This fact should account for the slow growth rate observed for films obtained under such experimental conditions (see Fig. 1(b)).

Finally we should observe that a general trend in the dynamical film composition is the development of oxidized Fe phases with increasing exposure time to laser radiation. The reactivity of freshly deposited Fe towards atmospheric oxygen, as well as the increasing oxygen up-take with densification of films during the growth process, should account for this behaviour.

In conclusion, the results obtained for thin films deposition by laser irradiating Fe(CO)₅ at two radiation wavelengths (248 nm and 488 nm) demonstrate the major influence of irradiation conditions on the growth rates, morphologies and chemical structure of films. For UV deposited films, higher deposition rates and lower C and O surface contamination were found. Using CW 488 nm radiation, a difference in C content of films deposited on Si relatively to SiO₂ substrates was evidenced.

The film properties were discussed in connection with experimental parameters and specific mechanisms involved.

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