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Implantation of xenon in amorphous carbon and silicon for brachytherapy application

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ABSTRACT

We report a procedure to implant high dose of xenon atoms (Xe) in amorphous carbon, a-C, and amorphous silicon, a-Si, for application in brachytherapy seeds. An ion beam assisted deposition (IBAD) system was used for the deposition of the films, where one ion gun was used for sputtering a carbon (or silicon) target, while the other ion gun was used to simultaneously bombard the growing film with a beam of xenon ion Xe^+ in the 0–300 eV range. Xe atoms were implanted into the film with concentration up to 5.5 at.%, obtained with Xe bombardment energy in the 50–150 eV range. X-ray absorption spectroscopy was used to investigate the local arrangement of the implanted Xe atoms through the Xe L_{III} absorption edge (4.75 keV). It was observed that Xe atoms tend to agglomerate in nanoclusters in a-C and are dispersed in a-Si.

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1. Introduction

Noble gases have been used in a number of applications in lasers, electronics and biomedicine [1–4]. Xenon (Xe) atoms have been incorporated in solid crystalline metals and semiconductors by ion implantation [5–7]. The xenon isotope ^{124}Xe has been proposed for potential application in brachytherapy, a cancer treatment technique based on invasive radiotherapy [8]. After neutron activation, ^{124}Xe (a non-radioactive Xe isotope) decays to ^{125}I , which emits beta radiation used to kill cancerous cells. The ^{125}I , a radioactive iodine isotope, is largely used in brachytherapy due to its low X-ray energy (<32 keV) and life-time of about 60 days [9–11]. In current brachytherapy treatment ^{125}I is obtained from liquid iodine. The radioactive ^{125}I is carefully introduced into a small biocompatible capsule, usually a titanium tube of few millimeter length and about one millimeter diameter [12,13], named brachytherapy seed. There are several techniques for introducing the ^{125}I into a capsule [9–11]. In cancer treatment, several capsules, with activity of about 0.3–0.8 mCi are introduced in the tumor.

During the fabrication of the ^{125}I seed, one has to handle radioactive material during the whole process, which is one of the disadvantages of the process. In this work we investigate the use of ^{125}I obtained from the transmutation of the ^{124}Xe gas (which is non-radioactive). In this case, one can introduced the ^{124}Xe into the seed through a physical process, without any special care concerning radiation. For the cancer treatment, ^{124}Xe must be introduced

in a thin film, which works as a host of the ^{124}Xe atoms. After neutron activation, the seeds are introduced into the body of the subject, inside the tumor, where the beta radiation kills the cancerous cells. The dose of radiation will depend on the amount of ^{124}Xe placed into the seed, and it must be sufficient to kill the cancerous cells. However, in order to achieve the right dose, a considerable large amount of Xe, of the order of 5–10 at.%, needs to be incorporated into a thin film. This process can be achieved by conventional implantation techniques, which adopts very high implantation energies, 10–100 keV. In conventional implantation Xe atoms are incorporated after the deposition of the film. In this work we propose the use of an ion beam assisted deposition (IBAD) system, a much simple technique, to incorporate large amount of noble gas, using very low energy (0–300 eV) during the deposition of the film. The process was investigated in two different matrixes, i.e., amorphous silicon, a-Si, and amorphous carbon, a-C.

2. Experimental

An IBAD system was used for the deposition of the a-C and a-Si thin films. One ion gun (Kaufman type) was used for sputtering a carbon, 99.99%, (or silicon, 99.999%) target, while the other ion gun was used to simultaneously bombard the growing film with a beam of xenon ion Xe^+ (99.999%) in the 0–300 eV range. In this process Xe atoms are implanted into the film, with thickness of approximately 70–100 nm, deposited at 150 °C on silicon substrate at a pressure of $\sim 5 \times 10^{-2}$ Pa. The system base pressure prior deposition was 10^{-5} Pa. A detailed description of the system is found elsewhere [14]. For this investigation, we used natural Xe, but for brachytherapy application it needs to be replaced by the isotope

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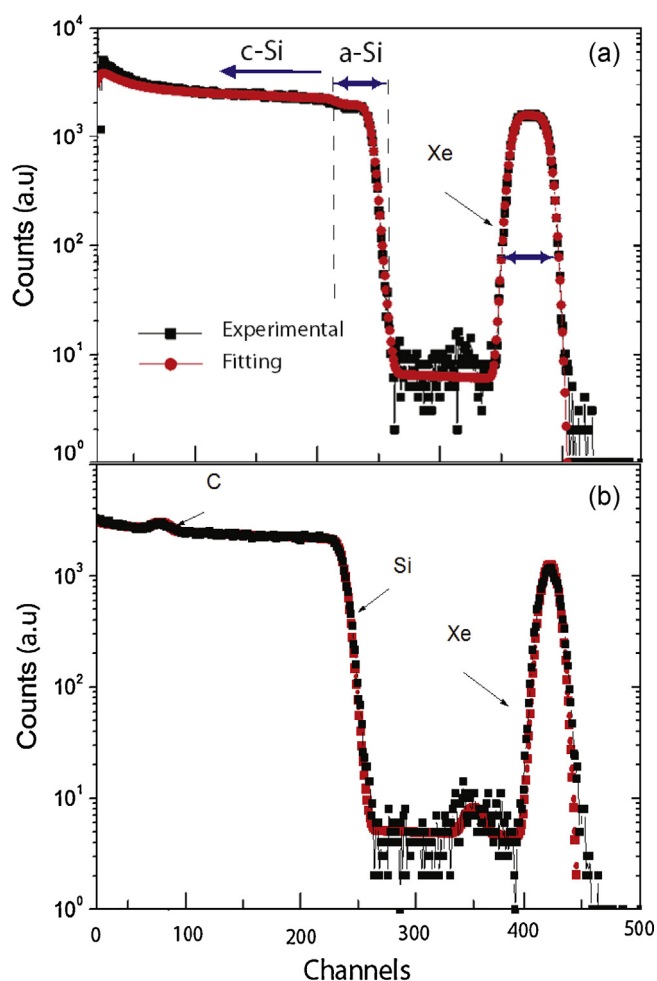


Fig. 1. RBS of a-Si(Xe) (a) and a-C(Xe) (b), showing the main features associated with the silicon substrate, a-Si and a-C thin film and the incorporated Xe atoms.

^{124}Xe . Since this gas is very expensive, we avoid using it, considering the results for its implantation must be the same. Electron energy loss spectroscopy (EELS) measurement indicated the a-C films are graphite-like, with 85% of sp^2 sites.

Rutherford backscattering spectroscopy (RBS) was carried out with He^+ beam energy of 2.2 MeV, charge of 40 μC , current of 60 nA and detection angle of 170° . The spectra were analyzed using the SIMNRA package [15]. X-ray photoemission spectroscopy (XPS) was carried out using Al $\text{K}\alpha$ radiation (1486.6 eV) at a pressure of 5×10^{-10} Torr with a VSH HA 100 analyzer. Stress measurements were performed using the bending beam method. In this technique one determines the radius of curvature of the film/substrate composite, which is used to supply the stress of the film using the Stoney's equation. A detailed description of the adopted apparatus and the procedure is described elsewhere [16]. X-ray absorption spectroscopy (XAS) of the Xe L_{III} edge (4.75 keV) was carried out in the X-ray beam line D04B-XAS at Laboratório Nacional de Luz Síncrotron (LNLS) in Campinas, Brazil. The measurements were performed with normal incidence light-beam and probing the total electron yield.

3. Results and discussion

Fig. 1 shows RBS spectra of Xe implanted in a-Si and in a-C, from now on also named a-Si(Xe) and a-C(Xe), respectively, to indicate the incorporation of Xe atoms in the film matrix. They show three main features. In Fig. 1(a) they are related to the c-Si substrate, the

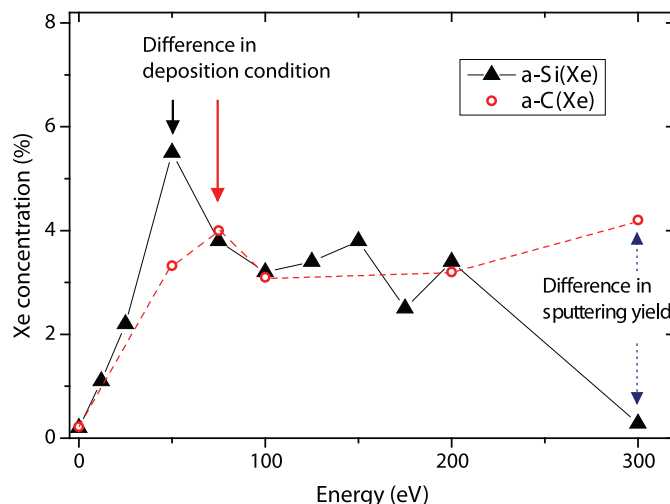


Fig. 2. Xe concentration in a-C and a-Si, as a function of Xe bombardment energy.

a-Si film and the incorporated Xe atoms. In Fig. 1(b) they also show the c-Si substrate and Xe, but the a-C film appears at low energy on top of the c-Si substrate signal, since the atomic mass of C is smaller than that of Si. The broad Xe-peak on both spectra indicates that Xe are homogeneously distributed along the film thickness. This is a great advantage when compared to conventional implantation, which is performed after the film deposition and not during the film deposition, as was done in this work. In addition, conventional implantation requires post annealing to reduce the defects created by the bombardment with high energetic ion beam. In the technique adopted here the annealing step is not necessary.

Fig. 2 displays the concentration of Xe obtained for the two series of film, a-C(Xe) and a-Si(Xe) by RBS, as a function of the Xe bombardment energy (or implantation energy). The two spectra are similar one to each other, but there are two small differences, indicated in Fig. 2. The concentration of Xe initially increases as the bombarding energy increases. This is in accordance with the model proposed by Davis and Robertson [17,18] and theoretically demonstrated by molecular dynamic [19]. The concentration reaches a maximum and then starts to decrease due to the thermal spike effect. The first difference is that the maximum are reached in different energies, as indicated by the two arrows in Fig. 2. This difference in energy is attributed to the conditions adopted in every deposition, such as the deposition rate, which are different for both materials. The other difference observed in Fig. 2 is related to the Xe concentration obtained with Xe energy bombardment of 300 eV. In this case, the concentration of Xe incorporated in a-C is much higher than the one incorporated in a-Si. That may be due to the sputtering effects caused by the bombardment with Xe atoms, which is also present during the deposition process together with the implantation of Xe atoms into the matrix. The sputtering yield of silicon is much higher than that of carbon, which can explain why the concentration of Xe is lower in the a-Si deposited at 300 eV.

The concentration of Xe in a-Si was also determined by XPS, but it is smaller than that obtained by RBS. However, it can be observed in Fig. 3 that there is a linear relation between both measurements. The difference is because XPS measures few layers on the top of the film. The concentration is smaller because the Xe atoms are implanted underneath a few layers from the surface and because Xe can easily be released from the surface of the film. The concentration determined by RBS is more reliable, since it represents the bulk of the film, while XPS probes the surface only.

To the best of our knowledge, conventional implantation of Xe in amorphous carbon and in amorphous silicon has not been reported

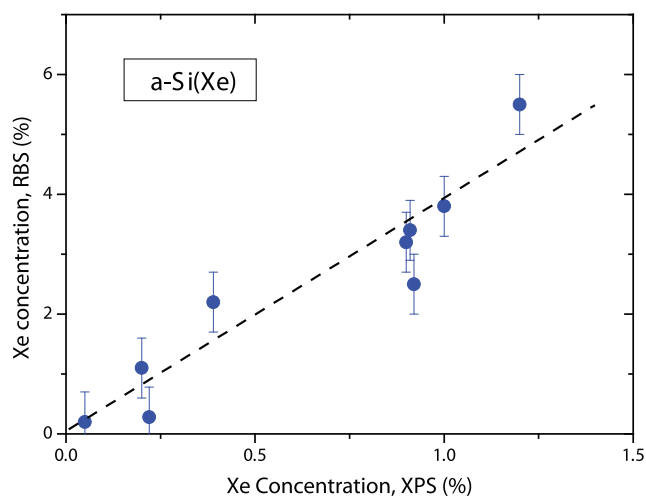


Fig. 3. Relation between the Xe concentration obtained by RBS vs. XPS in a-Si.

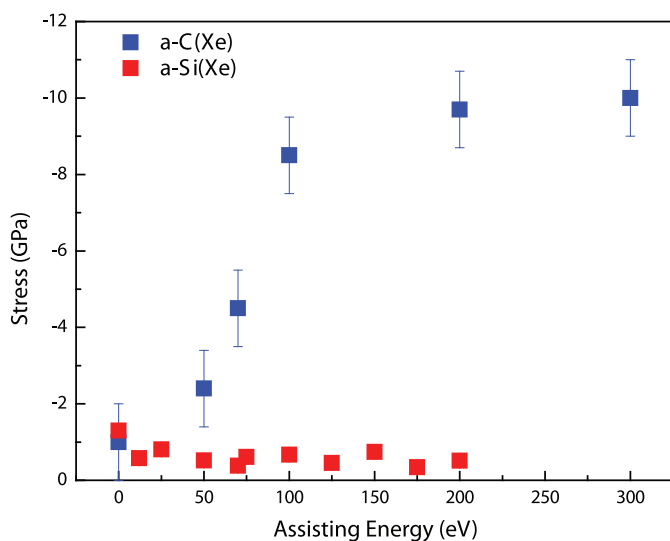


Fig. 4. Stress of the a-Si and a-C as a function of Xe bombardment energy.

by other researchers. In this work, the concentration of Xe incorporated by the IBAD technique is comparable to that obtained in other materials by conventional implantation [6,20,21]. However, there is an enormous difference in the Xe ion energy involved in both techniques. Usually, conventional implantation adopts ion energy >100 keV, while in this work the maximum concentration was achieved with only 50 eV (Fig. 2). This is a great advantage, since conventional implantation requires very expensive and complex equipment. Besides, the total Xe concentration incorporated into the films is comparable.

The bombarding process with Xe increases substantially the stress of the a-C films, Fig. 4. The stress reaches an extremely high value of 10 GPa with Xe bombardment energy in the 200–300 eV. On the other hand, the stress is smaller than 1 GPa for the a-Si films. This difference is attributed to the fact that the C–C bond is much stronger than the Si–Si bond. The stress of thin films is relaxed, with creation of bubbles, cracks and other defects, when the stress overcomes the bond strength between the atoms in the films. Thus, the highest stress achievable in a-Si must be smaller than that obtained in a-C, explaining the difference observed in Fig. 2.

An interesting effect observed in the a-C(Xe) films is the significant variation in the electrical resistivity of the film, as displayed in Fig. 5. The resistivity is reduced by 2 orders of magnitude as

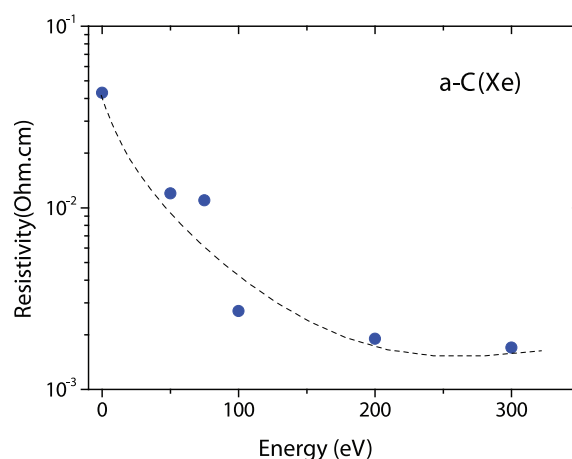


Fig. 5. Resistivity of the a-C(Xe) films as a function of the Xe bombardment energy.

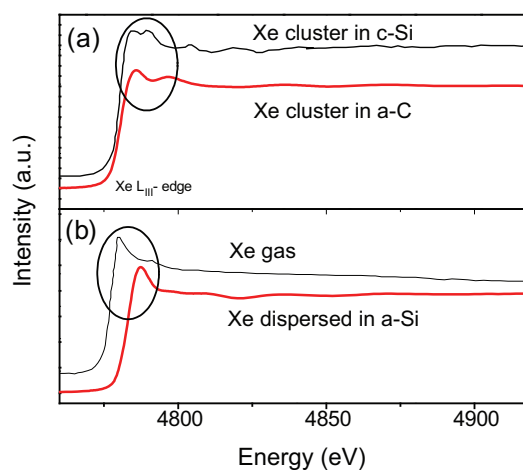


Fig. 6. XAS spectra of a-C (a) and a-Si (b), in red, and of Xe cluster in c-Si (a) and Xe gas (b), in black, included for comparison [20]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

the bombarding energy varies from 0 eV to 300 eV. This variation is probably related to a compression effect due to the high compressive stress of the film matrix, which changes the electronic band structure of the film. A similar effect has been observed in a-C incorporated with neon, argon and krypton [22]. No variation in the electrical resistivity was observed in the a-Si incorporated with xenon.

XAS measurement is a powerful tool to probe the local environment of some elements. Fig. 6 displays XAS spectra for Xe L_{III} absorption edge (4.75 keV) of the a-C (Fig. 6a) and a-Si films (Fig. 6b) with the highest concentration of Xe. XAS signal obtained from clusters of Xe in crystalline silicon (c-Si) (Fig. 6a) and from Xe gas (Fig. 6b) reported in literature [20], is included for comparison. The splitting of the white line into two peaks (Fig. 6a) is a characteristic feature associated with the formation of clusters, i.e., the presence of Xe–Xe bonds [14,20]. On the other hand, the absence of any feature in the white line, (Fig. 6b), indicates the presence of isolated Xe atoms. Thus, considering these characteristics, one can conclude that Xe atoms are found in cluster phase in a-C, while they are dispersed in a-Si matrix.

The formation of clusters in a-C must be related to two effects: (1) the graphite-like structure of the films, composed of clusters of graphene sheets, which supply space within the sheets for the formation of clusters due to some structural defects, and (2) the extremely high stress, 10 GPa, forcing the isolated Xe atoms within

graphene sheets to agglomerate themselves in a more favorable position. The presence of graphite clusters in amorphous carbon has been detected by Raman. Additional information concerning the presence of graphite-clusters in a-C and other structural properties can be found in a review paper by Robertson and references therein [23].

In Fig. 6 one can observe a shift in the Xe L_{III} absorption edge energy between all spectra. This difference is partially associated with the Xe environment (carbon or silicon). This phenomenon has been reported in other works [21]. In addition to that, there is a partial contribution due to experimental error and to the fact that both measurements were performed in different period of access to the synchrotron beam line.

4. Conclusion

The use of the ion beam assisted deposition (IBAD) technique, revealed a powerful tool to incorporate high dose of Xe atoms in a-C and a-Si matrix. Xe concentration of up to 5.5 at.% was achieved, which is appropriate to supply the right dose for the production of brachytherapy seeds. The maximum concentration obtained was about the same for both a-Si and a-C matrixes. However, the trapped sites are different. Xe atoms tend to agglomerate in nano-clusters in a-C and are dispersed in a-Si. This effect was attributed to a combined effect associated with the high stress achieved in a-C, up to 10 GPa, and with the graphite-like structure composed of large clusters of graphene sheets.

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