

SURFACE MODIFICATIONS OF FERROCENE USING ARGON ION  
IMPLANTATION AND  $\gamma$ -IRRADIATION

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The effect of  $\text{Ar}^+$ -ion implantation (energy 100 keV) has been studied on ferrocene pellets at  $1 \times 10^{14}$  and  $5 \times 10^{14}$  ions/cm<sup>2</sup> doses. The characterization techniques used were infrared spectroscopy, small-angle X-ray diffraction and bulk X-ray diffraction. At the lower dose, formation of a metastable alkene occurred; at the higher dose a metastable alkane was formed. The X-ray data showed that metastable phases like Fe-C  $\text{Fe}_2\text{C}$ , (Fe-C)H and carbon phases were produced at the surface. Not being observable on the surface, the organic counterparts are expected to be volatile in nature. When treated with varying energy doses, ferrocene showed bulk damage; the IR spectra showed the loss of fine structure and only a single peak persisted, which was due to metal-ring vibration.

## INTRODUCTION

Ion implantation and  $\gamma$ -irradiation are known techniques for influencing the physical and chemical properties of submicron layers below the material surface<sup>1-4</sup>.

The former is used as a powerful technique for surface modification of metallic, semi metallic and insulating systems. In such work one can obtain metastable phases having totally new features<sup>4</sup>. The metastable phases like iron carbides, due to their good thermal and mechanical properties, chemical inertness and low wear resistance<sup>5</sup>, find wide application particularly as wear-resistant materials. These are useful for protective coatings. In the case of ferrocene the bond between iron and the ring is comparatively weak; this is advantageous to obtain metastable phases of iron carbides. Introduction of such metastable inorganic phases otherwise appears to be difficult.

#### EXPERIMENTAL

Ferrocene has a sandwich structure. It is likely to exhibit semiconductor properties upon polymerization. From the readily available ferrocene powder, with a purity of 99.99%, pressed pellets of approximately 0.25 cm thickness were prepared using acetone as a binder and by applying approximately 7 ton pressure. The pellets were then wrapped in an aluminium foil. Before Ar<sup>+</sup> ion implantation a low angle XRD pattern was taken on a Rigaku (Japan) instrument, using CuK radiation at a grazing angle of 0.2°. Bulk XRD pattern was taken over the range of 2θ values from 5 to 45°. Medium energy ion implantation was carried out at an energy of 100 keV. The γ-irradiation was performed using a <sup>60</sup>Co source at a dose rate of 0.3 Mrad h<sup>-1</sup> over the dose range of 6-35 Mrad.

## RESULTS AND DISCUSSION

Small angle XRD patterns were obtained at  $\alpha = 0.2^\circ$ . The choice of this value was based on the consideration of X-ray penetration depth in the sample. When the pellet was treated with a dose of  $1 \times 10^{14}$   $\text{Ar}^+$  ion/ $\text{cm}^2$ , the small angle XRD pattern showed cracking of ferrocene molecules and synthesis of iron carbides like  $\text{Fe}_2\text{C}$ ,  $\text{Fe-C}$  and also a few carbon phases. Further, along with ferrocene as a major phase, some other phases of  $\text{Fe}_2\text{O}_3$  and  $(\text{Fe-C})\text{H}$  are formed. When treated with a higher dose of  $5 \times 10^{14}$  ions/ $\text{cm}^2$ , again, along with ferrocene as the major phase some phases of  $(\text{Fe-C})\text{H}$ ,  $\text{Fe}_2\text{O}_3$  and carbon phases appeared. Production of  $(\text{Fe-C})\text{H}$  phases was found to be larger than that of the  $\text{Fe-C}$  phases. The probable organic counterparts like acetylene, butadiene, etc., as indicated by the IR data, are absent in the surface layers. It is expected that such phases being volatile in nature must have evaporated off the surface. Similar observations were made in the case of organic polymers<sup>6-9</sup>. (Fig. 1)

Scrapings of the surface of the ferrocene pellet exposed to different doses were collected and a weighed amount was brought into pellet form in a KBr matrix. Figure 2 shows the observed infrared spectra of such ferrocene exposed to different doses. Spectra (a) are for untreated ferrocene, while spectra (b) and (c) are for samples exposed to  $1 \times 10^{14}$  and  $5 \times 10^{14}$   $\text{Ar}^+$  ions/ $\text{cm}^2$ , respectively.

It can be seen from spectra (b) that along with some bands of ferrocene a new peak at  $3000\text{--}2800$   $\text{cm}^{-1}$  appears; this may be an  $\text{sp}^3$  C-H alkane stretch; however, these peaks decrease to a large extent as the dose is increased. The peaks at  $1165$  and  $1460$   $\text{cm}^{-1}$

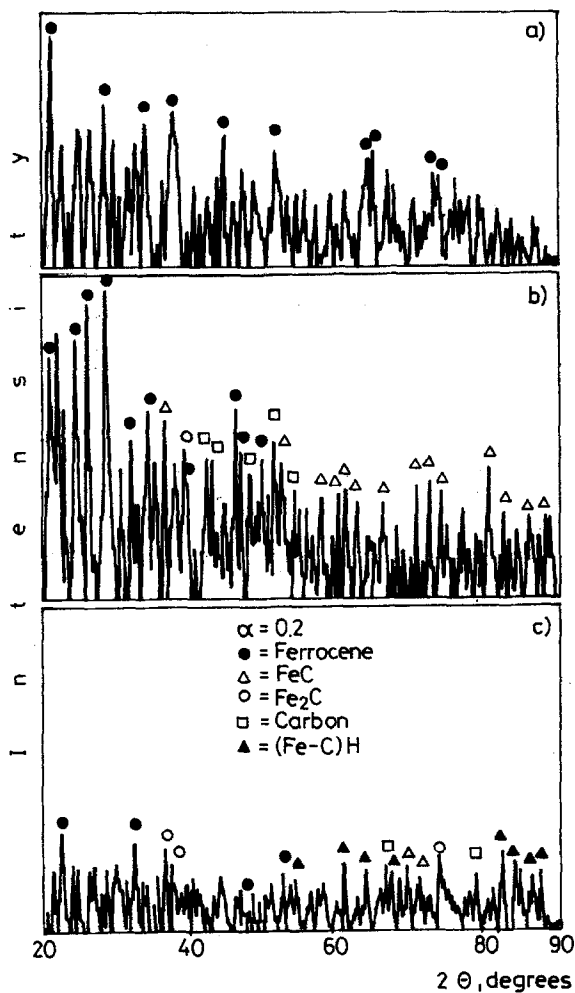


Fig. 1. Small angle XRD pattern for  $\text{Ar}^+$ -ion bombarded ferrocene at  $\alpha = 0.2^\circ$ : (a) untreated, (b) treated by a dose of  $1 \times 10^{14}$  ions/cm<sup>2</sup> and (c) by a dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup>

confirm the  $\text{sp}^3$  C-H alkane bend. Further, the peak at  $970 \text{ cm}^{-1}$  indicates the presence of trans-olefin compounds. Figure 2(c) shows the IR spectrum of ferrocene  $\text{Ar}^+$ -ion implanted with a dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup>. It in-

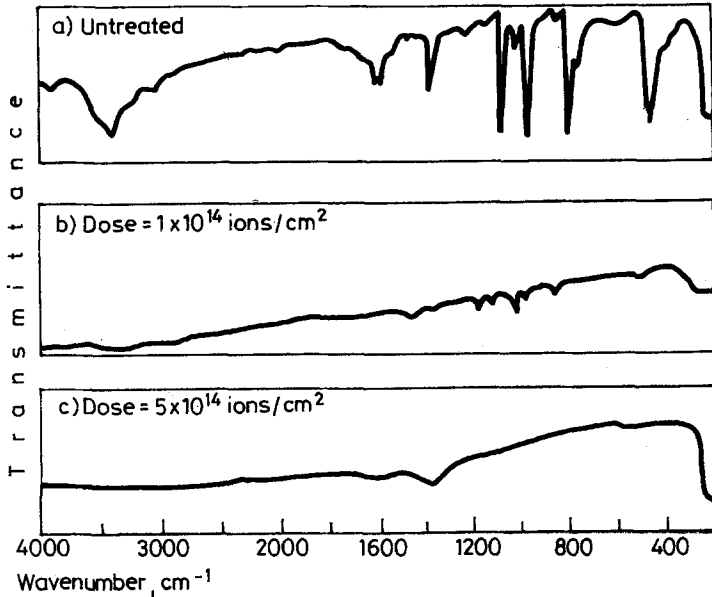


Fig. 2. Infrared spectra of ion implanted ferrocene pellet prepared in KBr matrix: (a) untreated, (b) treated by a dose of  $1 \times 10^{14}$  ions/cm<sup>2</sup> and (c) by a dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup>

indicates one broad alkane band at  $1370\text{--}1440\text{ cm}^{-1}$  and a very weak band at  $819\text{ cm}^{-1}$  due to the perpendicular C-H bend of ferrocene. As the dose is increased the olefinic compound becomes saturated, which is seen from the presence of a C-H band and the absence of C=C bands for lower doses of implantation. At higher dose there is a possibility of total decomposition. As is seen from Fig. 3(c), the peak alkane C-C stretch is present above  $1370\text{--}1440\text{ cm}^{-1}$ .

The effect of  $\gamma$ -irradiation of ferrocene can be seen in Fig. 3, where Fig. 3(a) refers to unirradiated ferrocene, and Figs 3(b) and (c) to irradiated ferrocene at various doses in increasing order. It can be

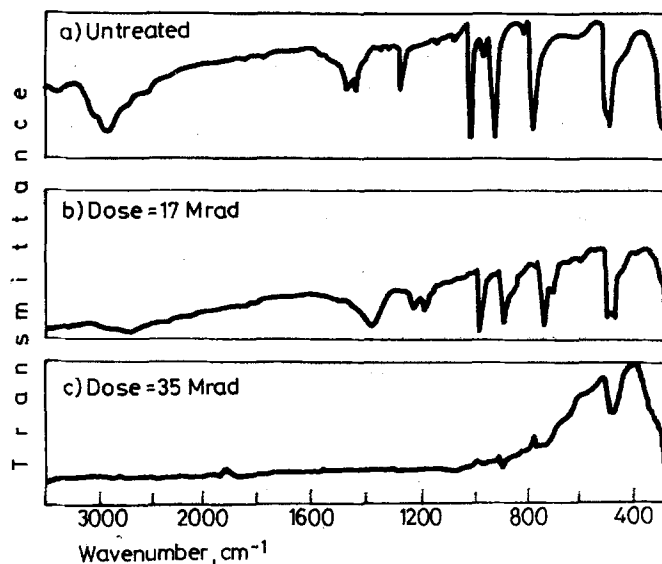


Fig. 3. Infrared spectra of a  $\gamma$ -irradiated ferrocene pellet prepared in KBr matrix: (a) untreated, (b) treated by a dose of 17 Mrad and (c) by a dose of 35 Mrad

seen from these figures that the weak bands at 3920, 3100, 2940, 2850, 2460, 2060, 1480 and 1040  $\text{cm}^{-1}$  are affected and nearly disappear, while those at 1610  $\text{cm}^{-1}$  1350-1370  $\text{cm}^{-1}$  become broad. Gradual changes are seen up to a dose of 17 Mrad, but at higher doses of 35 Mrad all vibration bands vanish, except for that between the metal and the ring. In general, the peak height is reduced, indicating that ferrocene is affected structurally throughout the bulk.

#### CONCLUSION

Both argon-ion implantation and  $\gamma$ -irradiation affect the surface structure of ferrocene. The  $\text{Ar}^+$  ions produce various phases like  $(\text{Fe-C})\text{H}$ ,  $(\text{Fe-C})$  and  $\text{Fe}_2\text{C}$ .

Some alkene compound forms at lower doses and a meta-stable alkane compound at higher doses.  $\gamma$ -Irradiation affects the bulk of the material and at very high doses total structural damage is observed.

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