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FRACTAL PATTERN GROWTH OF METAL ATOM CLUSTERS IN ION IMPLANTED POLYMERS*

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The fractal and multi-fractal patterns of metal atoms are observed in the surface layer and cross section of a metal ion implanted polymer using TEM and SEM for the first time. The surface structure in the metal ion implanted polyethylene terephthalane (PET) is the random fractal. Certain average quantities of the random geometric patterns contain self-similarity. Some growth origins appeared in the fractal pattern which has a dimension of 1.67. The network structure of the fractal patterns is formed in cross section, having a fractal dimension of 1.87. So it can be seen that the fractal pattern is three-dimensional space fractal. We also find the collision cascade fractal in the cross section of implanted nylon, which is similar to the collision cascade pattern in transverse view calculated by the TRIM computer program. Finally, the mechanism for the formation and growth of the fractal patterns during ion implantation is discussed.

Keywords: metal ion implantation, polymer, fractal pattern, multi fractal pattern
PACC: 3640, 6170, 6830

I. INTRODUCTION

The clustering of atoms and the formation of fractal patterns have become a new subject in solid state physics and material science. Fractal growth patterns, which manifest themselves in widely diverse fields, have been extensively studied over the past years. Current interest in fractal growth has been stimulated[1,2]. Recently, there seems to be an increasing interest in studying real fractal patterns, and there have been some papers published on pattern formation in thin solid films prepared by ion mixing[3–6]. But observations of fractal patterns in ion implanted polymers are comparatively few. Fractal geometry was introduced and developed for ion collision cascades in solids, and it can be applied in many different domains, including materials science[7,8].

In this paper, we present fractal and multi-fractal patterns in metal ion implanted polyethylene terephthalane (PET), and a new fractal structure similar to that observed in steel collision cascades is reported for the first time. The mechanism of fractal pattern formation in a polymer induced by metal ion implantation is discussed.

II. EXPERIMENTS AND METHODS

Specimens of PET with a thickness of 99μm and nylon wire were prepared for implantation. Ag, Cu, Ti and Ni ions were implanted with a metal vapour vacuum arc (MEVVA) implanter at an acceleration voltage of 40 keV and an ion flux of 4.5μA/cm^2. The ions in three charge states were extracted from the MEVVA implanter. The average charge states of Ag, Cu, Ti and Ni are 1.98, 1.99, 2.14 and 1.72, respectively. Several implanting doses were selected between 5×10^{15}/cm^2 to 2×10^{17}/cm^2. The cross-section structure of the sample is observed by transmission electron microscopy (TEM). The TEM cross-section samples were prepared by embedding the PET in epoxyresin and cutting into cross-sectional slices of 70–100nm thickness. The precipitation phases were detected using x-ray diffraction (XRD) and electron diffraction. After corrosion of implanted PET in an organic solution, scanning electron microscopy (SEM) and TEM observations of the surface structure of the sample were carried out.

III. RESULTS AND DISCUSSION

A. Formation of dispersed phases and fractal pattern growth

After corrosion of the implanted PET in an organic solution, the precipitation phases were revealed

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and a new morphology of the sample was observed by SEM. The substrate was dissolved in an organic solution after a corrosion time of over two hours. Only the implanted layer was left, so we can obtain the structure and electron diffraction pattern of the implanted structure with TEM. The results are shown in Figs.1, 2 and 3.

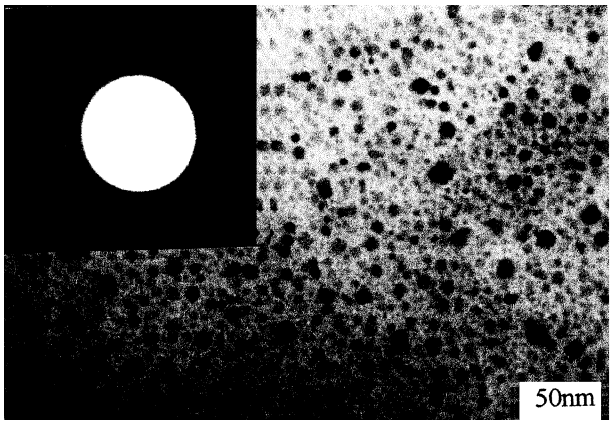


Fig.1. TEM photo of Ti implanted PET ($5\times10^{16}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

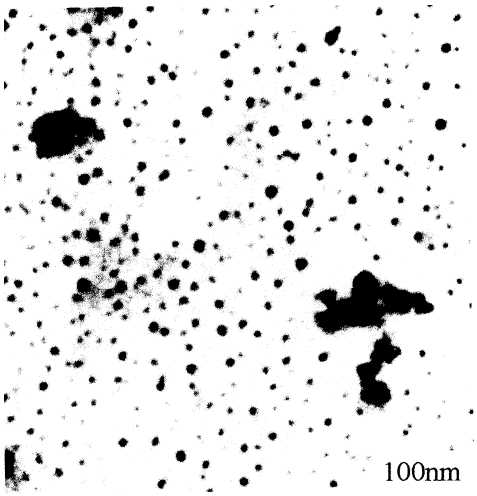


Fig.2. Nucleation and growth of metal atom precipitates in Ni implanted PET ($1\times10^{17}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

TEM examination reveals that the atomic rearrangement resulted in the agglomeration of metal atoms. The structure and electron diffraction pattern of Ti implanted PET to a dose of $1\times10^{17}/cm^2$ are shown in Fig.1. It can be seen that a spherical dispersed phase is uniformly distributed in the implanted layer. The size range of the particles is from 5nm to 20nm, with an average size of 15nm. Many smaller particles are distributed randomly in the open area around the nano-phase. The Ti atom flux is entering the spherical phase, which means that the spherical phase is growing. The electron diffraction pattern in the top left corner of Fig.1 shows that the precipitated phases consist of metallic Ti and Ti oxides. The implanted metal atom in PET diffuses and nucleates to form a new phase, and the phase grows during implantation. The nucleation and growth of precipitates depend sensitively on the ion implantation parameters, such as target temperature, dose and ion flux. The experiments indicate that the precipitate evolution is controlled in part by processes which are known to occur in supersaturated solid solution, radiation enhanced diffusion, recoil dissolution, localized solute enrichment or depletion near the sinks. Localized metal atoms enrich near the sinks so that high metal atom concentration is created in these regions. The nucleation and growth of metal atom precipitates occurred at lattice defects, sinks and dislocations as shown in Figs.1 and 2. These processes are active primarily during implantation. The precipitates are uniformly distributed due to the random distribution of the sinks. These processes are enhanced when the ion dose and ion flux increases. Therefore the aggregates of two particles and small fractal patterns are observed in Fig.2.

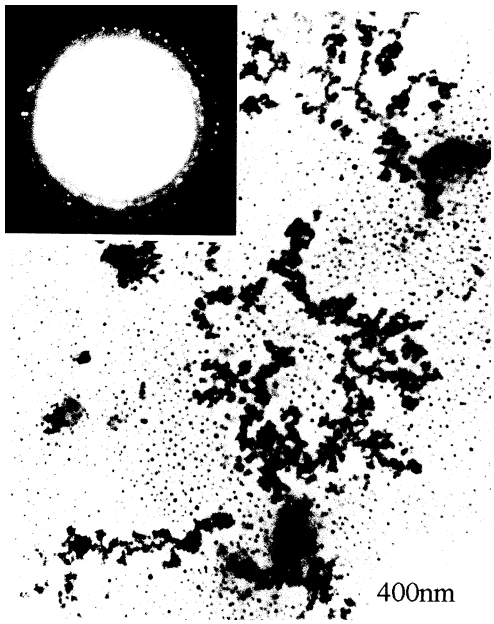


Fig.3. Fractal patterns in Ni implanted PET ($2\times10^{17}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

B. Fractal growth pattern

Fractal patterns were grown when the Ni dose of $2\times10^{17}/cm^2$ was used to implant, as shown in Fig.3. The fractal pattern with an average size of $2.2\mu m$

is composed of 50–70nm dark particles that generally line up in particular ways. Lined-up particles form the tree branches. The large clusters are chain-like. There are also many flower-like clusters located on the branches of the tree. These dimensions are qualitatively in agreement with those reported in the literature[7]. Plenty of smaller particles with sizes ranging from 5nm to 20nm are distributed randomly in the open area around the tree branches. From the density of the distribution of these smaller particles, it is clearly seen that the density around the branches is lower than that elsewhere, showing that smaller particles around the branches have moved into the branches to aggregate. In order to unravel the self-similar feature of this sort of pattern, the fractal dimension of 1.67 was measured from Fig.3 using a computer program. The observed patterns look similar in some aspects to those stipulated by the cluster-diffusion-limited-aggregation (CDLA) model[8]. According to this model, growth begins by the occupation of part of the available sites (such as sinks) and the positioning of a seed at the origin. The occupied sites are visualized as particles that remain fixed, while the growing clusters go through a random walk gathering up the fixed particles. The formation process of ion-induced fractal patterns in PET involves the formation of stationary large clusters and the motion of small species. Besides, long-range correlation is probably necessary for the formation of fractals in PET. The dense branching pattern is easily formed in PET, the reason is thought to be due to the behaviour of the microscopic structure of the PET. Anyway, this issue still needs more study, both experimental and theoretical. The electron diffraction analysis indicated that the fractal component is metallic Ni (see top left corner in Fig.3).

C. Embedded multi-fractal pattern formation

We have found a new multi-fractal structure composed of smaller nano-particles, 5–10nm in size, embedded in the open area of the original fractal pattern of large nano-particles. The new fractal pattern has the disconnected tree morphology as shown in Figs.4(a) and (b). The new fractal was formed in PET when the Ni ion dose increased, and is similar to that in Ref.[9]. These clusters also exhibit a local chain structure, and can therefore be formed by a similar mechanism. An essential feature of this new fractal pattern is the discontinuity of the pattern components. The sharp diffraction spots of the electron diffraction pattern further confirmed that the small precipitated particle is metallic Ni (see Fig.3). It has been demonstrated that the dimension of particles and the fractal pattern increase with increasing ion dose.

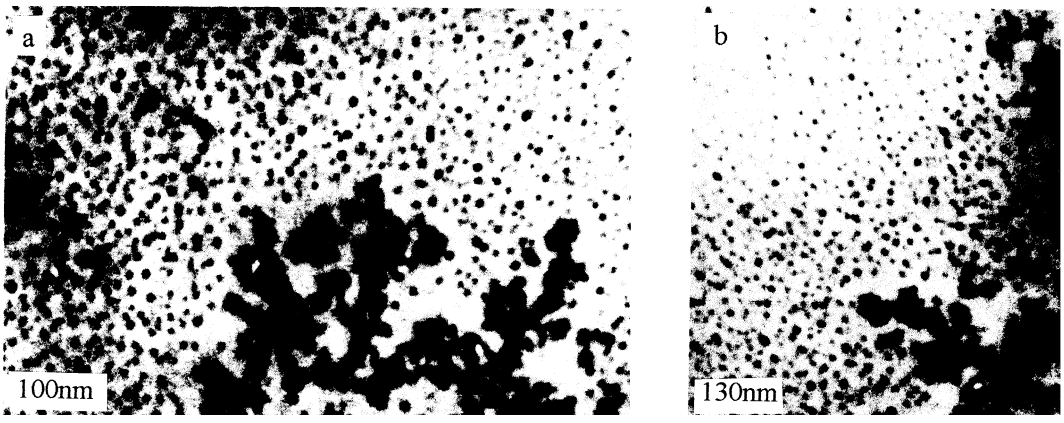


Fig.4. Embedded multi-fractal pattern formation in Ni implanted PET ($2\times10^{17}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

D. Three-dimensional fractal patterns

The cross-section TEM images of Cu and Ag implanted PET are shown in Fig.5. The main feature of each image is an implanted modified layer and the PET substrate. The thicknesses of the Cu and Ag modified layers are 240nm and 170nm, respectively. The interesting result is the fractal pattern formation in the cross section of the implanted sample. The compact branches of the fractal patterns are distributed in the narrow cross section of the sample. Comparing with the results of the foregoing experiments, we believe that three-dimensional fractal patterns are formed in the implanted layer in both cases.

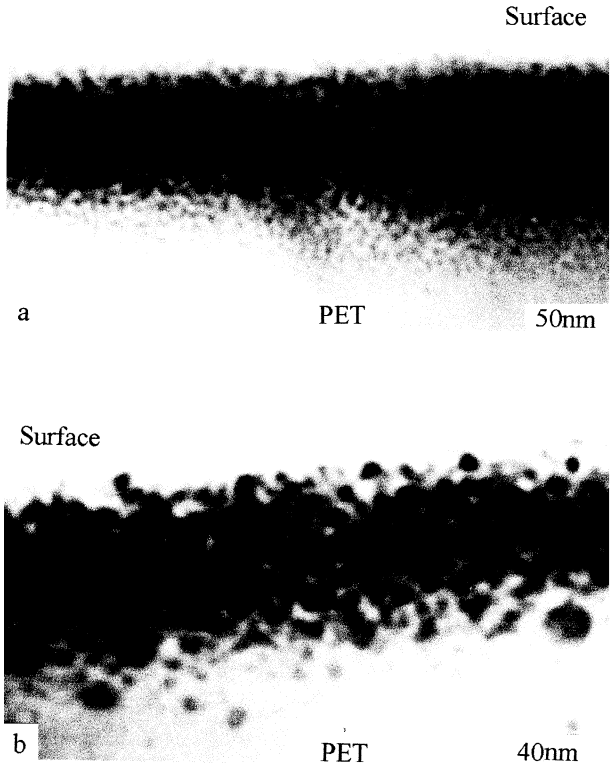


Fig.5. Three-dimensional fractal patterns in Cu (a) and Ag (b) implanted PET ($2\times10^{17}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

E. The collision cascade fractal pattern

Atom cascades in solids are considered as an idealized fractal geometry. Each branching point of a tree represents a binary collision event, and each branch corresponds to a mean free path of a displaced atom, as shown in Fig.6.[10,11] Fig.6 shows Ni ion collision cascade patterns calculated with the TRIM program. Fig.6(a) shows the longitudinal profile of the collision cascade. Fig.6(b) shows the transverse view of the collision cascade. But, until now, the collision cascade fractal pattern has been not observed. Recently, we obtained the collision cascade fractal pattern in Ni implanted nylon yarn, as shown in Fig.7. The dimension of the large pattern is about $2\mu m$, and that of the smaller pattern is about 300nm. The dimension of the small fractal pattern approximately equals the size of the calculated pattern in Fig.6(b). The patterns look like beautiful trees. The patterns also contain self-similarity. The origin of the fractal can be seen from Fig.7. The large pattern is formed by the collision of many ions. The small pattern is formed by one or two ion collisions.

Thermal spike effects of ion collisions in the polymer play an important role in fractal formation and growth. The nanometre clusters have diffused and aggregated into a chain to form tree branches and beautiful trees. The growth of metal clusters is effectively several factors of ion implantation, such as metal species, ion energy, ion dose, ion flux, target temperature and substrate species. A key parameter influencing the surface atom migration and aggregation is the cascade collision level and target temperature. Strength of cascade collision relies on ion dose. Therefore, the foregoing results show that the metal atoms coalesce into a cluster whose size and shape changes as a function of ion dose. The metal clusters precipitate to nanometre phases. The fractal increases when the ion dose further increases.

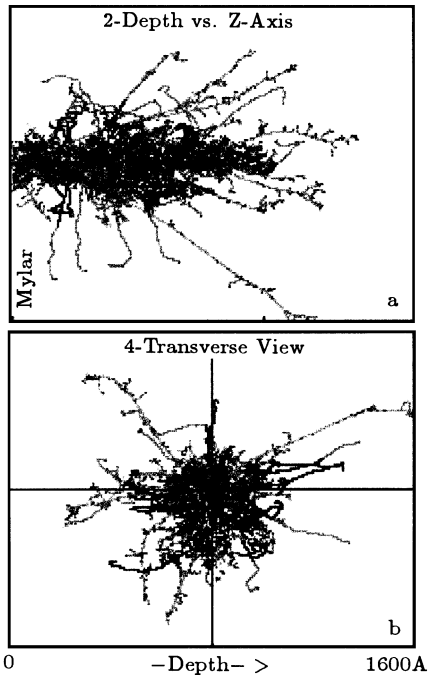


Fig.6. Collision cascade patterns of Ni implanted PET ($2\times10^{17}/cm^2$, 69keV) calculated by the TRIM computer program.

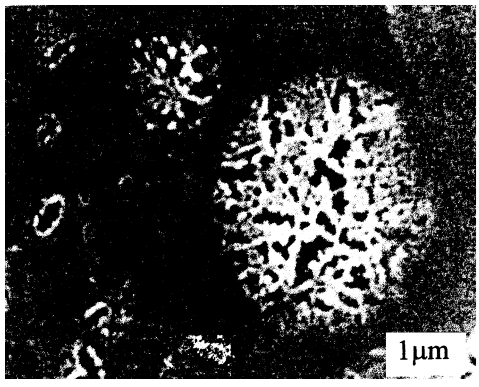


Fig.7. The collision cascade fractal pattern in Ni implanted nylon ($2\times10^{17}/cm^2$, 69keV) with an ion flux of $4.5\mu A/cm^2$.

IV. SUMMARY

Using metal ion implantation as an experimental tool, we have demonstrated the influence of ion dose on metal atom precipitation and fractal growth in a polymer induced by ion implantation. Our main results are summarized as follows.

(1) The fractal patterns of implanted metal atoms are observed in the surface and cross section of ion implanted PET for the first time. The surface structure in the implanted PET is the random fractal. Certain average quantities of the random geometric patterns contain self-similarity. One or more growth origins on the fractal pattern appeared. The fractal dimension of Ni implanted PET is 1.67.

(2) The network structure of the fractal patterns is formed in the cross section of Ag implanted PET. The fractal dimension is 1.87.

(3) The fractal pattern is three-dimensional space fractal.

(4) A new fractal structure, namely the embedded multi-fractal pattern, has been observed.

(5) The collision cascade fractal in the cross section of implanted nylon is similar to the collision cascade pattern in the transverse view calculated by the TRIM computer program.

(6) Thermal spike effects of ion collision in the polymer play an important role in formation and growth of fractals.

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