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LETTER TO THE EDITOR

Two-dimensional chain structures observed in carbon-ion-implanted nickel thin films

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Abstract. Two-dimensional polycrystalline chain structures were observed in carbon-ion-implanted nickel thin films. The significant excluded-volume effect led to a randomly folded highly polydisperse configuration, as compared with the random coil model in three dimensions. Individual chains had a fractal dimension ranging from 1.24 to 1.45, depending on whether they exhibited linear or branching behaviour as related to the local growth environment. A microscopic feature of the chain structure was a sausage-like aggregation of polycrystals, which was attributed to the dense distribution of polycrystals and to the requirement of reduced surface energy.

The configurations of macromolecule chains have been studied extensively using model systems approximating the random walk, such as freely jointed chains, freely rotating chains, and chains with rotational potentials [1]. The specific conformation adopted by a macromolecule may be determined from the bond lengths, bond angles and rotations about the bonds. Under normal conditions—e.g. at room temperature—states of different bond lengths, and/or angles, and/or rotations may be easily transformed into each other because of the small difference in conformation energy. The ease of such transference leads to the chains taking on a great diversity of forms, and the random walk model is applicable. Because two atoms cannot occupy the same position, this model is more accurately referred to as the random coil model in the literature. In real solutions, the coil often swells or collapses to some extent, depending on the solvent, with the fractal dimension varying from $5/3$ to 3 [2]. At the theta point these effects disappear and the ideal random coil model holds. In the case of amorphous solids, Flory concluded that the random coil picture would be the appropriate model for the polymer state; that is, no swelling or collapse would be induced [3]. This model also leads to a mean field of density. However, Yeh suggested a two-phase model to take into account the microscopic density fluctuation [4].

The distinct properties of chains related to the space dimension—such as the fractal dimension and the excluded-volume effect—were intimately related to the critical

phenomena [5]. The condition for polymerization, $N \rightarrow \infty$, corresponds to $\epsilon \rightarrow 0$ in critical theory [6]. To test the theory, experimental results, especially for two dimensions, are still needed, although a vast amount of work for three dimensions has been compiled (see, e.g., [7]). Recently, aggregation of magnetic microspheres in water, and computer simulations have produced two-dimensional chain structures [8]. The fractal dimension may change from 1.41 ± 0.02 to 1.23 ± 0.12 , depending on the magnetic dipolar interaction. Ion irradiation has proved to be uniquely valuable for studying condensed matter phenomena in two dimensions, because of the ease of control of the experimental parameters, e.g. the ion beam energy, flux, and dose [9]. In this letter, we report the formation of a two-dimensional chain structure in ion-implanted metal thin films.

The experimental procedure is as follows. Pure metal Ni thin films were deposited onto freshly cleaved NaCl in an electron gun evaporation system. The vacuum was better than 2×10^{-6} Torr. The thicknesses of the films were designed by TRIM-88 to match the 50 keV carbon-ion range plus longitudinal straggling. The as-deposited films were then implanted at room temperature under flowing water cooling in a vacuum better than 5×10^{-6} Torr. The ion beam current density was kept below $1 \mu\text{A cm}^{-2}$ to minimize the heating effect. We defocused the ion beam to obtain a continuous spread at a fixed average dose. The implanted films were then analysed with a JEOL 100CX transmission electron microscope (TEM) and a Perkin-Elmer scanning auger electron microscope (AES).

Figure 1 shows the patterns observed after implantation to an average dose of $2.5 \times 10^{17} \text{ cm}^{-2}$, at which the phase transition was expected to take place. A TEM selected-area diffraction pattern is shown in figure 2, and this confirms the formation of the hexagonal carbide Ni_3C . The AES spectra measured at different depths showed the coexistence of amorphous carbon and polycrystalline carbide as 'fingered' from the carbon KLL lines group [10], shown in figure 3. Existence of amorphous nickel was also indicated by the stoichiometry of the carbide and the relative peak-to-peak heights of carbon versus nickel. The analysis results were that about 25% of the C was in the carbide while 75% remained in the amorphous bonding, and that about 60% of the Ni was in the carbide while 40% remained in the amorphous state. The possible positions of carbon atoms in the hexagon were the octahedral interstices. There were two carbons in one hexagon forming the stoichiometry of Ni_3C . The interaction among the crystals may be realized from the strong covalent binding via carbon atoms; the magnetic force can be estimated from the distance between Ni atoms according to the Bethe curve [11], and the always existing van der Waals forces.

It has been predicted theoretically that the excluded-volume effect is stronger in two dimensions than in three. The excluded-volume effect may be estimated from

$$(R - R_0)/R_0 \propto (N^v - N^{1/2})/N^{1/2}$$

where R is the real end-to-end distance of the chain of N monomers. $R_0 = aN^{1/2}$ is the end-to-end distance of an ideal random coil with average effective bond length a . If we take R to be that of a self-avoiding random walk, then $R = aN^v$, where the critical exponent v is related to the space dimension by $v = 3/(d + 2)$. Then the theoretical prediction may be verified and the excluded-volume effect may even disappear in four dimensions.

The fractal dimension of the chains was analysed by digitizing the image using a VAX-M75 computer system with a resolution of 512×512 pixels and calculated by the box-counting method [12]. Either by the segment method for a linear chain or by the square-grid method for a branching chain, the fractal dimensions, D , were found to be

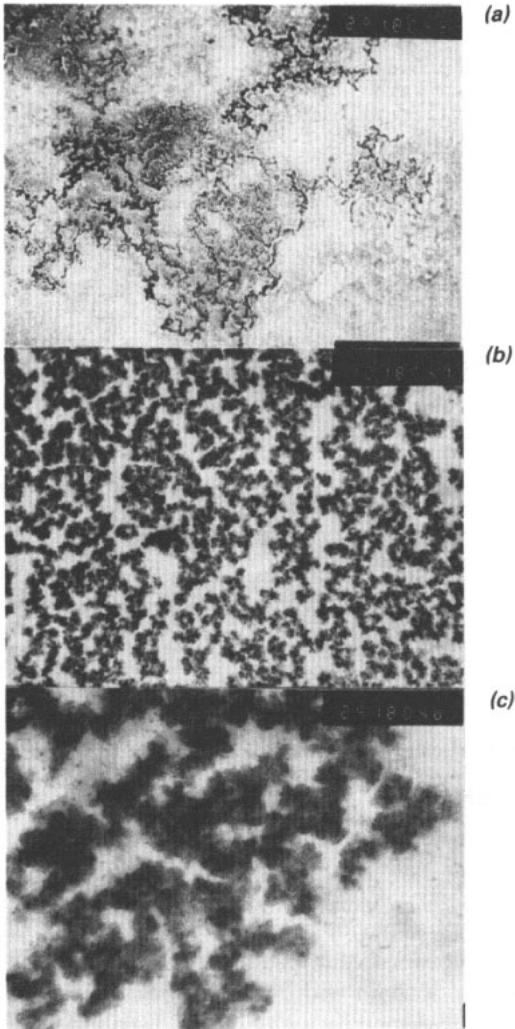


Figure 1. (a) The observed macro-polycrystalline chains in the carbon-ion-implanted nickel thin film at a dose of about $2.5 \times 10^{17} \text{ cm}^{-2}$. (b) The fully developed randomly folded configuration of chains in the matrix. (c) The fine structures of the macro-polycrystalline chain. Magnifications: (a) 2.9×10^3 ; (b) 10^4 ; (c) 2.9×10^4 .

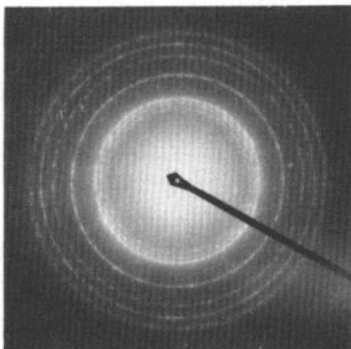


Figure 2. The electron diffraction pattern of the nickel carbide formed under carbon-ion implantation to a dose of $2.5 \times 10^{17} \text{ cm}^{-2}$.

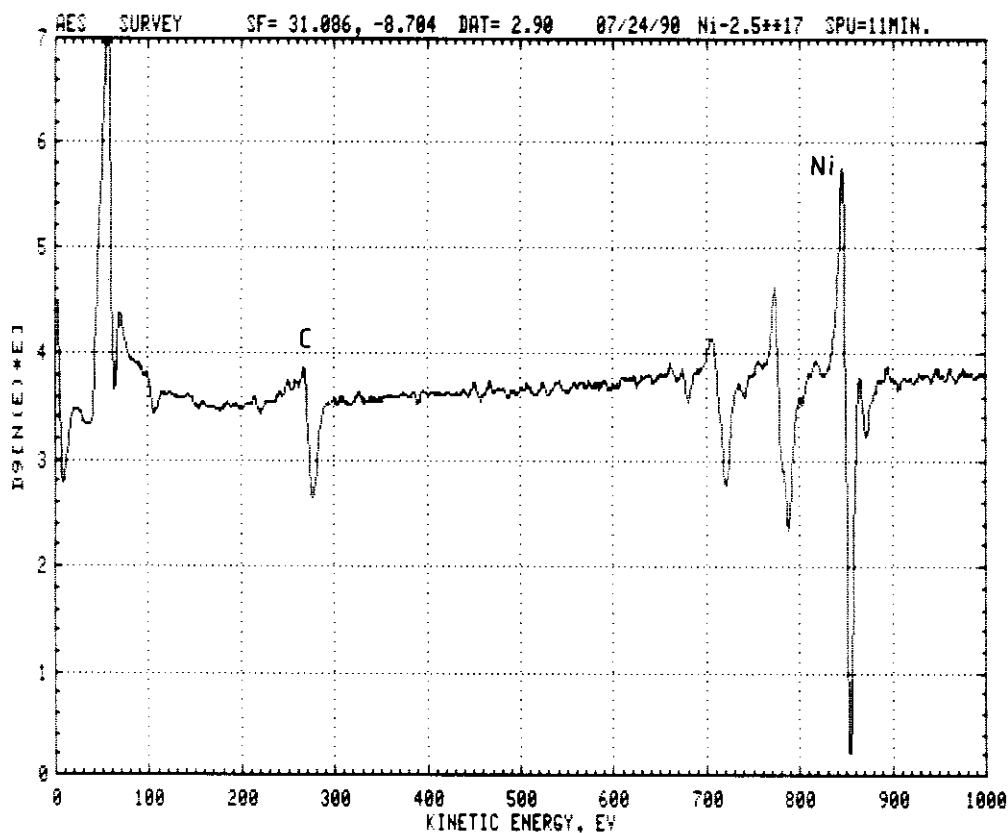


Figure 3. A typical Auger electron spectrum at a dose of $2.5 \times 10^{17} \text{ cm}^{-2}$.

between 1.24 and 1.45. The fractal dimension of a specific chain is related to the local growth environment conditions. Because of the significant excluded-volume effect in two dimensions, the nucleation and growth of a chain within the area of developed chains will be depressed, which leads to high polydispersity with a broad distribution of N ; otherwise branching or grafting will be enhanced, which will lead to a higher fractal dimension. For the chain growing in a relatively free space, the fractal dimension was around 1.32, approximately the same as the value for the self-avoiding random walk ($4/3$). Thus the fractal dimension can tell us something about the local environment conditions for growth.

As stated above, the solid state of the polymer in three dimensions can be described by the exact random coil model. To reach this point, the polymers must be highly entangled with each other or themselves. However, in two dimensions, growth by entanglement was impossible. This led to an ultimate configuration of randomly folded and highly polydisperse chains, as shown in figure 1(b). The observed density fluctuations suggest the two-phase identification [4] to be valid.

The fine structure of the chain is exhibited in figure 1(c). It is characterized by the sausage-like aggregation of polycrystals. The size of each polycrystal is about 100–200 Å which was the typical size of polycrystals formed in the ion beam process. By aggregation to the shape of a sausage, the surface energy between the inner domain and the outer region will be decreased and this leads to a more stable structure. In polymers, this is

often accomplished via coiled coils (see, e.g., [7]), such as the DNA double helix, or collapse to balance thermal instability [13]. Density fluctuations, which are important in the non-equilibrium implantation process, greatly affected the local aggregation of polycrystals. The dense distribution of polycrystals favours the formation of a sausage configuration. The process of macroscopic chain structure formation most probably proceeded via microscopic polycrystalline aggregation.

In conclusion, this study showed the formation of macro-polycrystalline chain structures via the process of ion-solid interaction in two dimensions. The distinct features of the two-dimensional chains were the enhanced excluded-volume effect and the formation of a randomly folded and highly polydispersive configuration as compared to the random coil model in three dimensions. The fractal dimension may tell us something about the local environment for growth. Besides this, microscopic features of the chain provide information on the process of chain structure formation by aggregation.

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