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Surface morphology, structure, magnetic and electrical transport properties of reactive sputtered polycrystalline $Ti_{1-x}Fe_xN$ films

X.C. Wang [a,*], W.B. Mi [b], G.F. Chen [c], X.M. Chen [a], B.H. Yang [a]

[a] Tianjin Key Laboratory of Film Electronic & Communicate Devices, School of Electronics Information Engineering, Tianjin University of Technology, Tianjin 300191, PR China
[b] Tianjin Key laboratory of Low Dimensional Materials Physics and Preparing Technology, Institute of Advanced Materials Physics, Faculty of Science, Tianjin University, Tianjin 300072, PR China
[c] School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China

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A B S T R A C T

Polycrystalline $Ti_{1-x}Fe_xN$ films with different Fe atomic fractions (x) were fabricated by reactive facing-target sputtering. The lattice orientation changes from (2 0 0) to (1 1 1) with the increase of x, which makes the surface morphology evolve from spherical, triangular-pyramid-like islands to random-leafs-like ones. The films are ferromagnetic with a Curie temperature of higher than 305 K, and the saturation magnetization (M_s) is very small. Obvious asymmetric M–H curves are observed at low temperatures, and the shift of M–H curves decreases with the increasing temperature because of the relaxation of the pinned moments at low temperatures. All of the samples show semiconducting-like behavior with a mechanism of variable-range hopping at low-temperature range. Magnetoresistance (MR) is very small. The small M_s and MR can be explained by the facts that the interaction between Fe^{3+}–N^{3-}–Fe^{3+} is antiferromagnetic superexchange coupling, and no double exchange exists in Fe^{3+}–N^{3-}–Ti^{3+}, which is different from that in the Cr-doped TiN films.

1. Introduction

Titanium nitride (TiN) is a transition-metal compound showing covalent and ionic properties, which makes its unique physical, chemical and mechanical characteristics such as good corrosion resistance, biocompatibility, high elastic modulus, yield strength and fracture toughness [1,2]. Thus, it is very interesting for both practical applications and fundamental research [3]. Calculations show that the chemical bonding in TiN has a covalent characteristic that is the reason for the high hardness and brittleness, high melting point (2950 °C), and resistance to corrosion [3–5]. The high-temperature ferromagnetism of 3d element-doped ZnO, TiO_2, SnO_2 and GaN semiconductors was observed frequently and it is found that the ferromagnetic properties are related to the defects and density of carriers [6–11]. Generally, the resistivity of ZnO, TiO_2, SnO_2, GaN etc. is high enough, but TiN has a higher density of carriers. Therefore, if the 3d elements were doped into TiN, the films should show different magnetic and electrical transport properties.

Inumaru et al. reports that the electrical transport and magnetic properties of the $Ti_{1-x}Cr_xN$ epitaxial films and solid solutions with relative large Cr atomic fraction, where the Curie temperature of 140 K is lower than room temperature [12,13]. Alling investigated the magnetic properties of $Ti_{1-x}Cr_xN$ solid solutions using first-principles calculations [14], and found that the magnetic interactions between Cr spins that favor antiferromagnetism in CrN is changed upon alloying with TiN, leading to the ferromagnetism in the system at approximately $x \leq 0.50$, which is in agreement with the experimental results [12–14]. Mi et al. fabricated the polycrystalline $Ti_{1-x}Cr_xN$ films using reactive sputtering, and found that the films are ferromagnetic with a Curie temperature above 305 K and MR shows a weak saturation trend with the applied magnetic field, and increases greatly with the decreasing temperature below 50 K following a relation of $\log\left|MR\right| = a - bT^{1/2}$ [15]. It is well known that CrN is an antiferromagnet and has the same lattice structure with TiN. The ferromagnetic characteristic comes from the double exchange coupling between Cr–N–Cr(Ti) chains. However, no double exchange coupling will appear in Fe^{3+}–N^{3-}–Ti^{3+}, and the interaction between Fe^{3+}–N^{3-}–Fe^{3+} is antiferromagnetic superexchange coupling. Thus it will be different that Fe was doped in TiN lattice. In this paper, polycrystalline $Ti_{1-x}Fe_xN$ films with

* Corresponding author.
E-mail address: wangxccn@126.com (X.C. Wang).

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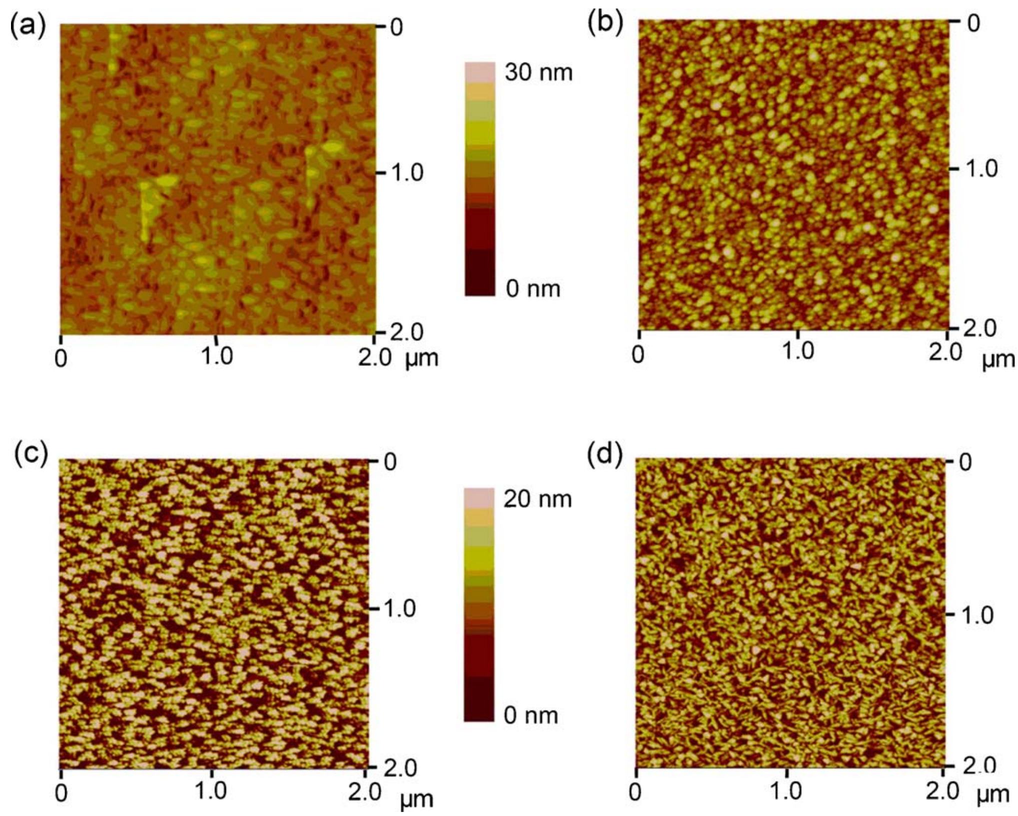

Fig. 1. AFM images of the polycrystalline $Ti_{1-x}Fe_xN$ films with different x, (a) 0, (b) 0.04, (c) 0.15 and (d) 0.43.

different x were fabricated. The surface morphology, structure, magnetic and electrical transport properties were investigated systematically.

2. Experimental details

Polycrystalline $Ti_{1-x}Fe_xN$ films with different Fe atomic fractions x ranging from 0 to 0.43 were fabricated by reactive facing-target sputtering in the Ar (99.999%) and N_2 (99.999%) gas mixture on glass and kapton^{TM}. In our facing-target apparatus, two targets with the same size were arranged with parallel facing their planes. The magnetic field is applied perpendicular to the target surface in order to confine the high energy charged particles and focus the plasma in the space between the two faced target planes. The distance between two targets with a diameter of 100 mm was 100 mm. The substrates were placed at the perpendicular bisector of the two targets, and the substrate plane was parallel to the axis of the two targets with a distance of 80 mm. The substrate was not heated. The sputtering was carried out from a pair of pure Ti (99.99%) targets on which pure Fe (99.9%) chips were fixed. The sputtering power was set at 210 W. Fe atomic fraction was changed by varying the number of Fe chips. The base pressure was better than 1.0×10^{-4} Pa, and the total pressure of the sputtering gas was kept at 1.0 Pa with Ar (15 sccm) and N_2 (15 sccm) flow rates. The film thickness was ~400 nm determined by a Dektak 6M surface profiler. The surface morphology of the films on glass substrates was measured using atomic force microscopy (AFM, Nanoscope IV) and scanning electron microscopy (SEM, TDCLS4800). The atomic fraction of the elements in the films was measured using an energy dispersive X-ray spectrometer (EDX) equipped on the SEM. The lattice structure was characterized by X-ray diffractometer (XRD, D/max-2500×, Cu Kα, wavelength 0.1504 nm). Quantum Design physical property measurement system (PPMS–9) was used to measure the magnetic and electrical transport properties at temperatures ranging from 2 to 305 K. The films on the Kapton^{TM} were used to magnetic measurements and those on glass substrates were used to electrical properties measurements with standard four-probe methods.

3. Results and discussion

Fig. 1 shows the AFM images of polycrystalline $Ti_{1-x}Fe_xN$ films with different x. At $x = 0$, the large islands on the film surface can be observed, and the island size on the film surface is about 100 nm. The shape of the islands is ellipse. At $x = 0.04$, the island size becomes small, and reaches about 30 nm. The shape of the islands is circular. As x increases to 0.15, some small islands contact with each other, and form big ones, which look like a "flower". When x increases to 0.43, the island shape was changed and looks like the "leafs". By comparing the AFM images, one can see that the details of the surface morphology can be observed in Fig. 1(c) and (d), which suggests that the rounded islands in Fig. 1(a) and (b) should not be from the AFM tip shape. The different surface morphology may arise from the differences of the lattice orientations of the grains on the film surface. All of the [1 1 1] oriented films have a microstructure that all of the grains point to a corner upwards, while all of the [2 0 0] oriented films have a rather smooth, curved surface. All of the random oriented films exhibit a plane upwards microstructure [16–18]. The leafs-like surface morphology should be the results of the coexistence of [1 1 1] and [2 0 0] oriented grains. The above mentioned relation between surface morphology and lattice orientation can be confirmed by the following XRD results. In general, the average surface roughness R_a is defined as the arithmetic average deviation from the mean line within the assessment length L [19]. The average surface roughness is 1.549, 3.476, 4.898 and 3.301 nm at $x = 0$, 0.04, 0.15, and 0.43, respectively.