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ARTICLE

Interdiffusion and Interaction Associated Microstructure Evolution Between Fe-Co Thin Film and Al_2O_3 Substrate

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Abstract: By advanced analytical transmission electron microscope, an unexpected interdiffusion between magnetron sputtered Fe-Co thin film and Al_2O_3 substrate was detected and systematically investigated in this study. Results show that a new phase of spinel $FeAl_2O_4$ forms, leading to the formation of interfacial layer. Detailed microstructure characterization reveals the interdiffusion associated with incommensurate structure formation near the interface in the Fe-Co thin film. The interdiffusion and accompanied new phase formation between the Fe-Co thin film and sapphire substrate are detected, and the associated microstructure evolution at the interfacial region is discussed, which may considerably influence the thin film magnetic properties.

Key words: Fe-Co alloy; interdiffusion; interface; microstructure; transmission electron microscope

The ferromagnetic Fe_xCo_{1-x} alloy has attracted many interests in the field of fundamental science and technologic applications, i.e., data storage and high-performance transformers, due to its high saturation magnetization, low coercivity, high Curie temperature (>820 °C), and large variations in magnetic properties with different composition[1-4]. Particularly, the Fe_xo_{1-x} alloy with high Curie temperature attracts attention for high temperature applications, such as aircraft electrical generators. Various high temperature applications require that Fe_xo_{1-x} alloy is able to sustain high induction and has good thermal stability under stringent operation conditions. The prerequisite for obtaining alloys with such high performance is that the alloy should have ideal microstructure and stability of constituent phases.

Nevertheless, it is difficult to well control the structure of Fe-Co alloy during preparation and operation processes. A large amount of studies investigated possible phase transformation in Fe-Co system at different temperatures. It is reported that the face center cubic (fcc) based Fe-Co alloys (austenite) transforms into body center cubic (bcc) based Fe-Co alloys (ferrite) when the temperature decreases. At low temperature, the Fe-Co system suffers an order-disorder transformation between B2 ordered and bcc disordered phases[5,6]. The composition change and related microstructure evolution observed in Fe_xCo_{1-x} grains considerably influence the structural stability and magnetic properties[7,8]. For example, the sign of the first crystal anisotropy constant changes as the Co content increases in the bulk Fe_xCo_{1-x} alloy[9]. Besides, the composition or structural change in Fe_xCo_{1-x} alloy films also alters the magnetic properties, as reported in the results of Fe_xCo_{1-x}/ZnSe and Fe_xo_{1-x}/MgO materials systems[10,11].

In addition, the interdiffusion or interaction between ferromagnetic alloys and substrates/composites was also reported. For instance, some investigations of the annealed or high-temperature-deposited thin film Sm-Co/Fe samples demonstrate the interfacial mixing of Co with Fe[12,13]. However, the possible interfacial mixing or reacting between Fe-Co thin film and sapphire substrate is barely comprehensively studied so far. This is mainly attributed to the strong thermal and chemical stability of Al_2O_3, which is a widely used insulator material for oxide ceramics and electronics industry[14]. It is hence believed that the reactions between Fe-Co films and insulator substrates, i.e., sapphire, are few or negligible. Nevertheless, the study of the interface between Fe-Co thin film and insulator

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SiO_2 substrate demonstrates that an unexpected interfacial reactions occurs in the metal-insulator system[15]. Moreover, the interdiffusion between sapphire substrate and other films, such as n-GaN, was reported[16].

To address this issue, the possible interfacial reaction between Fe-Co thin film and sapphire insulator substrate was investigated in this study by analytical transmission electron microscopy (TEM). The interdiffusion was quantitatively characterized, and a new phase arising from the interaction between Fe-Co thin film and Al_2O_3 substrate was detected. The accompanied microstructure evolution at the interface was elucidated accordingly.

1 Experiment

Thin film Fe_xCo_{1-x} binary samples (thickness ~200 nm) were deposited on sapphire substrate with (0001) orientation at room temperature with the ultra-high vacuum (UHV) magnetron sputtering system under a base pressure of 10^{-8} Pa[17]. The target was Fe-Co alloy with 60wt% Fe and 40wt% Co. The deposition rate was about 5 nm/min. The as-deposited samples were then annealed at 800 °C for 3 h under the UHV condition.

The annealed samples were then prepared for the cross-sectional TEM observations by sticking two identical annealed Fe_xCo_{1-x} samples face-to-face, followed by traditional TEM sample preparation procedure, i.e., mechanical thinning, grinding, dimpling and final ion-milling in a precision ion polishing system to obtain the electron-transparent thin area.

The TEM observations were performed on JEOL JEM 3010 and FEI Titan 80-300 analytical instruments at 300 kV. The FEI Titan TEM is also equipped with a high-angle annular dark-field (HAADF) detector and an energy-dispersive X-ray spectrometer (EDS) which can work under both TEM and scanning transmission electron microscopy (STEM) modes. The STEM-EDX spectra were acquired with sample stage tilted of 15° toward the X-ray detector to ensure the optimal counting rates, and the EDS results were used to analyze the quantitative composition across the film-substrate interface.

2 Results and Discussion

Fig.1 shows the STEM bright filed (BF) and dark field (DF) images of the cross-sectional polycrystalline Fe-Co thin film on the sapphire substrate. Besides the Fe-Co film and the Al_2O_3 substrate, a complete interfacial layer is observed especially from the STEM-DF image. Since Fig. 1b is obtained through the high angle scattering electrons, the local composition variation is observed clearly. However, it cannot be determined that such an interfacial layer is a Fe-Co layer forming at the beginning of deposition, or a new phase arising from the possible interaction between the thin film and substrate. In order to confirm the features of interfacial layer, detailed microstructure characterization and elemental spatial distributions at the interfacial region were then analyzed.

Fig.2a is the TEM-BF image of Fe-Co grain observed along [001] zone axis (ZA) with darker contrast compared to nearby off-zone axis grains. The corresponding selected area electron diffraction (SAED) pattern is shown in Fig.2b, indicating the crystalline phase of the grain. By indexing the diffraction pattern, the grain phase can be determined as Fe-Co with B2 structure, which is an ordered bcc structure and generally regarded as the simple cubic lattices interwoven with each other[18,19]. Interestingly, in the SAED pattern taken from both the Fe-Co grain and the interfacial layer (Fig.2c), extra diffraction spots can be seen accordingly, besides the sharp diffraction spots of Fe-Co grain with B2 structure. The corresponding DF image of the extra diffraction spot marked by a circle in Fig.2c is shown in Fig.2d, which clearly confirms the existence of an interfacial layer with different phases from the Fe-Co thin film and Al_2O_3 substrate.

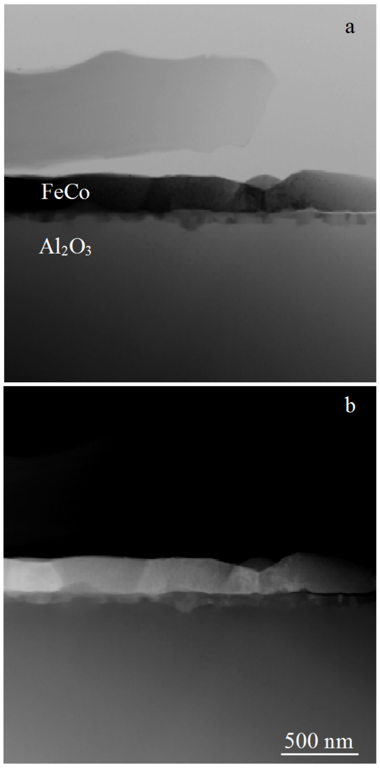

Fig.1 STEM bright field (a) and dark field (b) images of cross-sectional Fe-Co thin film on Al_2O_3 substrate

The interfacial layer consists of small randomly oriented grains. Fig. 3a is a TEM-BF image of Fe-Co grain along ZA [123]. Several SAED patterns acquired along the interfacial layer are shown in the insets of Fig.3b~3d, and different extra spots can be seen in these patterns. The small grains can be seen in the DF images by observing the extra spots in the insets.

For further understanding of element spatial distribution at the interfacial region, EDS analyses by STEM mode were conducted thereafter. Fig.4a is a STEM-BF image of Fe-Co grain and its underlying substrate. A series of STEM-EDS point scans were conducted accordingly as shown in Fig.4a, and the corresponding EDS spectra are presented in Fig. 4b. In the bulk Fe-Co grain far away from interface (point 1 and 2 in

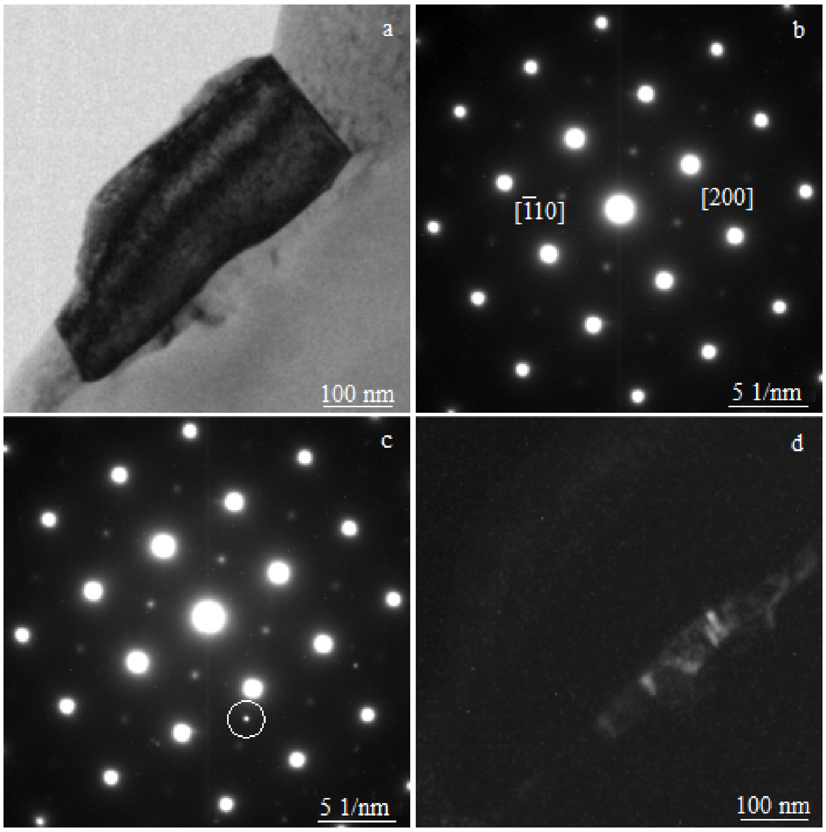

Fig.2 TEM-BF image (a) and corresponding SAED pattern along ZA [001] (b) of Fe-Co grain grown on Al_2O_3 substrate; SAED pattern of Fe-Co grain and interfacial layer (c); TEM-DF image of the spot marked in Fig.2c (d)

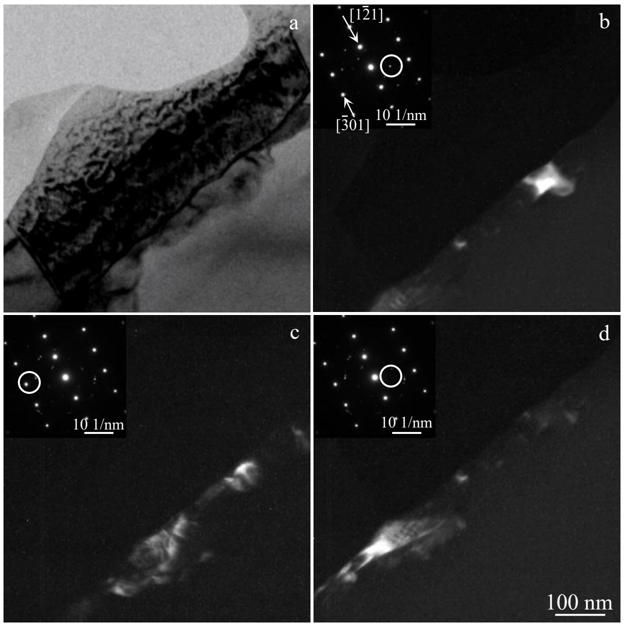

Fig.3 TEM-BF image of Fe-Co grain and interfacial layer (a); DF images of extra spots marked in the insets of corresponding SAED patterns along ZA [123] (b~d)

Fig. 4a), and only Fe and Co peaks can be detected (Fig. 4b). Whereas near the interface (point 3 in Fig. 4a), detectable Al and O peaks appear in the Fe-Co spectrum. At the substrate region far away from interface (point 6 in Fig. 4a), only Al and O can be detected. While at the substrate side near the interface, Fe/Co peaks begin to appear in Al_2O_3 spectra (points 4 and 5 in Fig. 4a). The atomic ratio between Fe and Al is about 1:2 which is determined at the center position of the interfacial layer (point 4 in Fig. 4a). The qualitative intensity evolution of different element peaks in EDS spectra across the interface indicates the status of intermixing element mass of Fe-Co grain with Al_2O_3 substrate. The intensity of Co peaks decreases more significantly than that of Fe at point 3 and 4. At point 5, there is still a weak Fe peak while Co peak cannot be detected anymore.

The element spatial distribution at the interface was also confirmed by STEM-EDS line scan across the interface. Fig. 4c is the STEM-DF image of Fe-Co grain on the sapphire substrate, and the STEM-EDS line scan was acquired across the interface. The corresponding concentrations are shown in Fig. 4d. The concentration of Fe and Co decreases gradually from Fe-Co side to sapphire substrate. For the counterpart, the Al and O elements in substrate also diffuse into Fe-Co grain. This subsequently results in the formation of intermixed layer

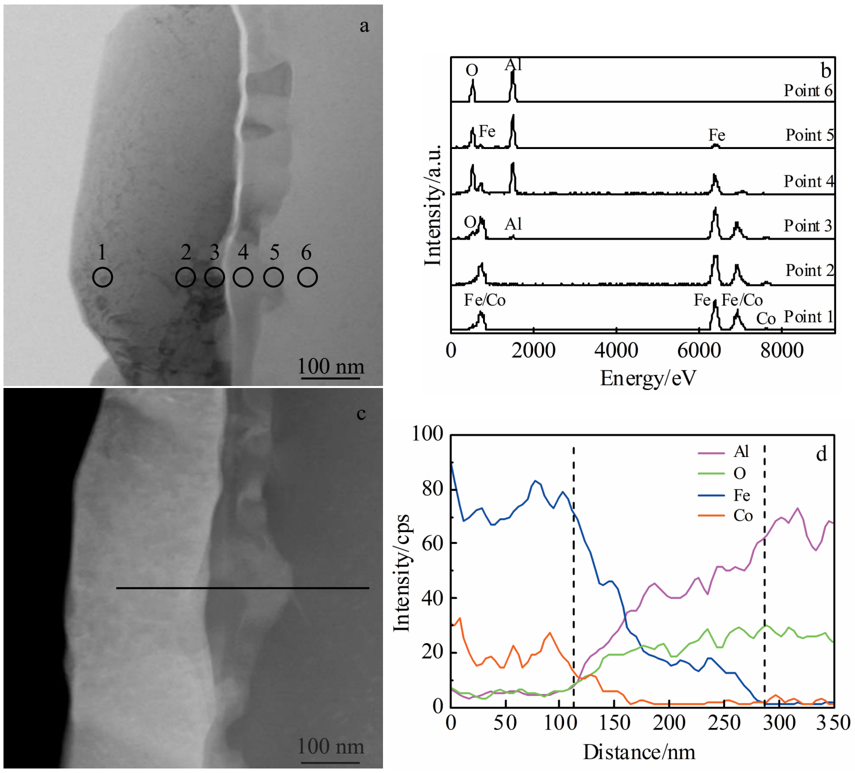

Fig.4 STEM-BF image of Fe-Co thin film on Al_2O_3 substrate (a); STEM-EDS spectra of different points in Fig.4a (b); STEM-DF image of Fe-Co thin film on Al_2O_3 substrate (c); STEM-EDS line scanning along marked line in Fig.4c across the interface (the dashed lines indicate the region which deviates from the initial homogenous composition) (d)

between thin film and substrate. The concentration of Co decreases faster than that of Fe at the interfacial region, which is similar to the STEM-EDS point scan results shown in Fig.4.

Since the interdiffusion results in the formation of interfacial layer, it is desirable to determine the newly appeared phase at the interface. Owing to the high activities of Fe and Al, various compounds form in the Fe-Al-O system. Several spinel-structured compounds, such as $A_{3-x}B_xO_4$ (x=0~2), form when the temperature is below 2000 °C[20,21]. According to the atomic ratio between Fe and Al in the interfacial layer, the interfacial phase is probably $FeAl_2O_4$ with spinel structure, which exists when the temperature is below 1780 °C. Then, the formation of $FeAl_2O_4$ is further confirmed by SAED. Fig. 5a is the TEM-BF image of typical Fe-Co grain with a clear underneath interfacial layer. The SAED pattern of the area marked in Fig. 5a is shown in Fig. 5b. The SAED pattern can be indexed in terms of the $FeAl_2O_4$ compound. It suggests that the interfacial layer formation is mainly attributed to the interdiffusion/interaction between Fe and Al_2O_3. Besides, it implies that Fe diffuses relatively faster than Co, or it is easier for Fe to intermix with Al_2O_3 so the new $FeAl_2O_4$ phase forms at the interface.

According to the detected interdiffusion accompanied with the formation of spinel $FeAl_2O_4$, Fe is enriched at the interfacial layer. Accordingly, it is believed that more Co remains in the Fe-Co thin film and Co is enriched in the initial homogeneous Fe-Co thin film near the interface, leading to the unbalanced Fe and Co concentration ratio, non-stoichiometry near the interface, and possible microstructure change. This is also supported by the fact that the width of region which deviates from the initial homogenous composition is larger than that of the interfacial layer. It is well known that the bcc-structured Fe is usually more stable than bcc-structured Co under ordinary condition. Consequently, the concentration of constituents shows considerable influence on the stability of bcc-structured Fe-Co materials[22,23].

Fig.6a shows the BF image of Fe-Co grain with underneath interfacial grains. The corresponding SAED patterns of Fe-Co thin film in the region near the interface are shown in Fig.6b and 6c. Fig.6b is the SAED pattern along ZA [001], which reflects the typical B2 structure. Interestingly, when the same Fe-Co grain is tilted to a different ZA [102] (as seen in Fig.6c), besides the diffraction features of B2 structure, other periodic diffraction spots appear as well. When this grain is further tilted to ZA [112] (Fig.6d) and ZA [133] (Fig.6e), extra periodic diffraction spots can still be observed, implying the formation of some ordered-structure in Fe-Co thin film. The SAED pattern with extra periodic diffractions, other than the diffraction of pure B2 structure, is orientation-dependent, which excludes the possibilities of microstructure changes due to oxidation of

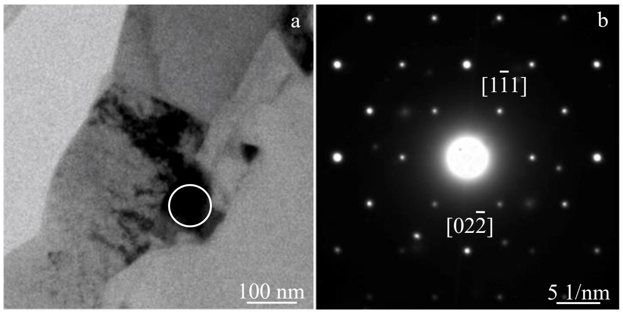

Fig.5 TEM-BF image of cross-sectional typical Fe-Co grain (a) and corresponding SAED pattern of the interfacial grain along ZA [011] (b)

surface or ion milling damage during the sample preparation.

The detailed structural features at atomic scale can be observed by high resolution transmission electron microscope (HRTEM). It is interesting that the typical bcc lattice can be seen in bulk Fe-Co far away from the interface (Fig. 7b). The corresponding SAED pattern obtained along ZA [111] only shows the diffraction spots from bcc lattice. Nevertheless, long-range ordered incommensurate structure can be observed in the film near the interface, as shown in Fig. 7c. The enveloped area is magnified, as shown in Fig. 7d. The inserted fast Fourier transformation (FFT) diffractogram indicates the formation of incommensurate structure in the bcc matrix. Such incommensurate structure originates from the long-range ordered bcc lattice. Fig. 7e is the invert fast Fourier transformation (IFFT) image of pure bcc lattice at the same region of Fig. 7d and the related FFT result is presented in the inset. If we block all the spots from the bcc lattice and only remain extra diffraction features, as shown in Fig. 7f, the IFFT image arising from the extra periodic diffraction spots can be obtained, which clearly represents the typical incommensurate structure. It confirms that due to the interdiffusion/interaction between Fe-Co and Al_2O_3, B2-structured Fe-Co evolves into the incommensurate structure with long-range ordering near the interface.

The Fe enrichment at the interface layer exists because of more Fe diffusion and accumulation near the interface, compared to the status of the counterpart Co, which is the predominant reason for the formation of incommensurate structure in the Fe-Co grain near the interface. It is manifested that Fe atoms can enhance the force constant values in the neighbor sites and stabilize surroundings in the bcc structure[24]. At the Fe-deficient Fe-Co region, it is thereby easier for lattice relaxation and rearrangement, leading to the incommensurate formation.

In the previous investigations, it is suggested that the magnetic properties of Fe_xCo_{1-x} alloy films can be considerably altered by both the composition and structure change[10,11]. Therefore, it is believed that such long-range ordered incommensurate structure plays a crucial role in determining the unique magnetic properties of Fe_xCo_{1-x} alloys. In addition, the quantitative STEM-EDS line scan results support the graded composition and non-stoichiometry around the interface due to the interdiffusion, which may also influence the magnetic properties of the system. But the effect extent of interdiffusion on bcc phase chemistry in this binary material is still unclear, which rises an interesting new topic and needs more detailed investigations.

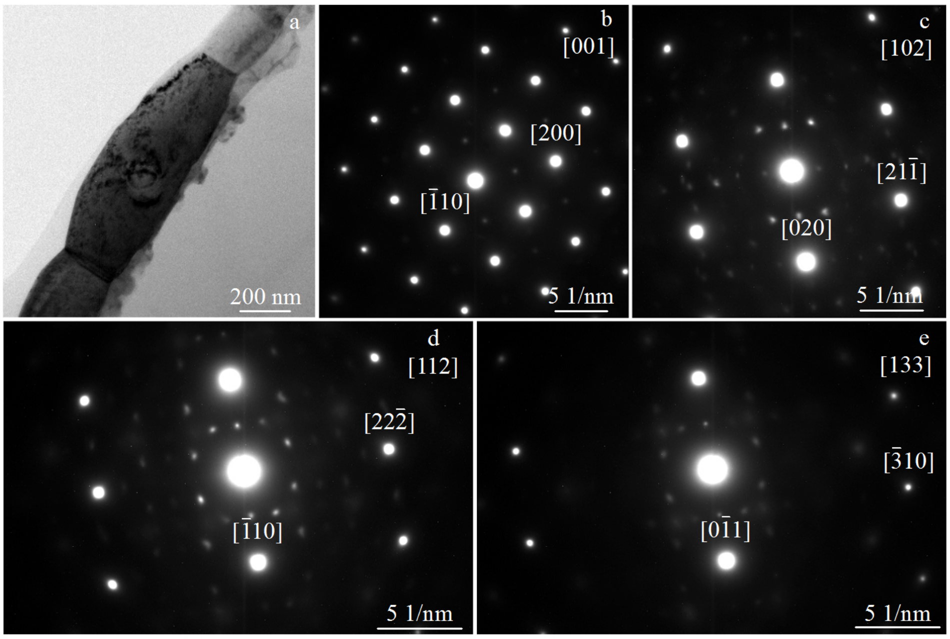

Fig.6 TEM-BF image of Fe-Co grain on Al_2O_3 substrate (a) and SAED patterns of the regions near the interface (b~e)

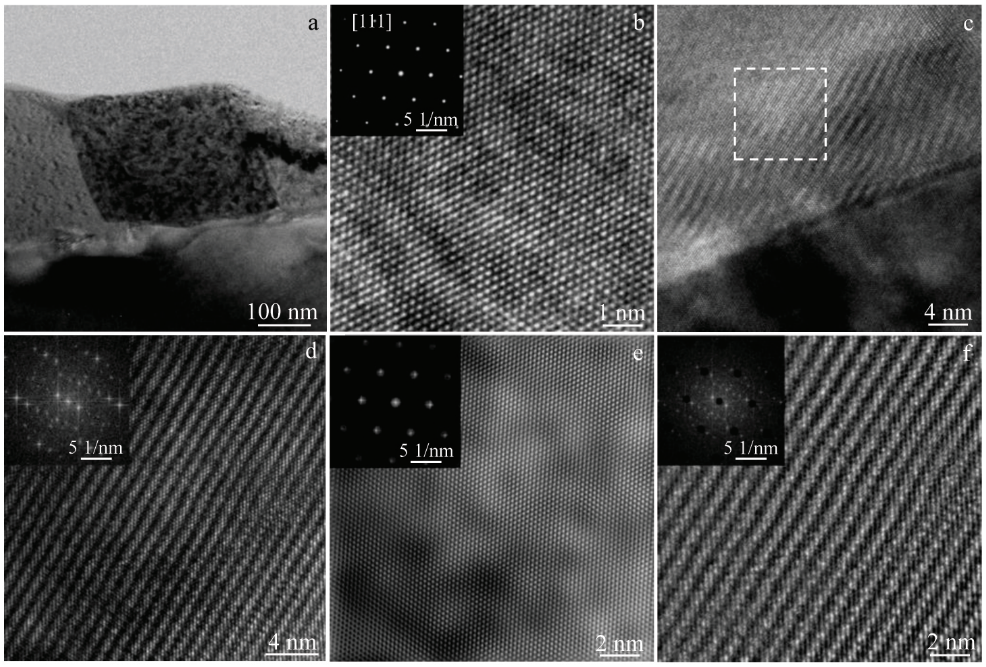

Fig.7 TEM-BF image of Fe-Co grain (a); HRTEM image with the corresponding SAED pattern along ZA [111] in inset of Fe-Co grain in the region about 0.1 μm from the interface (b); HRTEM image of Fe-Co grain in the vicinity of interface (c); magnified HRTEM image with the corresponding FFT diffractogram in the marked region of Fig.7c (d); IFFT images with the related FFT diffractograms in insets of bcc-structured Fe-Co (e) and extra diffraction feature (f)

3 Conclusions

1) The interdiffusion between Fe-Co thin film and Al_2O_3 substrate is detectable, leading to the formation of interfacial layer.

2) Quantitative STEM-EDS data provide clear measurement of elemental spatial distribution at the interface. Due to the Fe diffusion and accumulation, the new $FeAl_2O_4$ phase with spinel structure forms and is randomly oriented at the interface, resulting in the formation of interfacial layer.

3) Such interdiffusion/interaction, accompanied with Fe enrichment and non-stoichiometry of Fe-Co near the interface, leads to the microstructure evolution, i.e., the formation of incommensurate structure.

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Fe-Co薄膜与Al_2O_3基体相互扩散和相互作用相关的微观结构演变

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摘　要：利用先进分析透射电子显微镜，检测并系统地研究了磁控溅射Fe-Co薄膜与Al_2O_3基体之间的相互扩散。结果表明，扩散会形成尖晶石相$FeAl_2O_4$，并导致界面层的形成。微观结构表征表明，在界面附近的Fe-Co薄膜中形成了与相互扩散相关的非公度结构。本研究不仅检测到Fe-Co薄膜与蓝宝石基体之间的相互扩散和伴随的新相形成，而且揭示了界面区域相应的微观结构演变，这些结果可能对薄膜的磁学性质有很大的影响。

关键词：Fe-Co合金；相互扩散；界面；微观结构；透射电子显微镜

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