

분석전자현미경용 다층박막 디스크의 시편준비법

논 문
8-4-10

TEM Sample Preparation of Thin Film Multilayer Disks for Analytical Electron Microscopy

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요 약

메그네트론 스퍼터링으로 제작한 고밀도 다층박막 ($\text{Co}_{75}\text{Pt}_{12}\text{Cr}_{13}$ 합금) 디스크를 투과전자현미경을 이용해 단면 및 평면의 미세조직의 조사 혹은 미소부위 성분분석을 할 경우, 선행되어야 하는 시편준비 경로와 각 단계별 구체적방법 및 그 효과를 연구하였다. Ion 밀링 시간이 증가함에 따라 시료가 얇게 되는 과정에서 스퍼터링된 물질이 관찰될 시편부위의 다른 표면에 증착됨으로써 미세조직의 선명도를 해칠 수 있고, 이로 인한 해석상의 오류가능성이 시사되었다. 또한, 자기박막 디스크와 같이 다층으로 구성된 단면분석용 시료에서는 서로 맞붙인 실리콘 단결정 접착면을 따라 밀링속도가 선택적으로 커서 우선축이 생김으로써 양질의 시편을 얻기 어려운 문제점이 제기되었다. 이 같은 문제를 포함한 전자현미경 시료준비 과정에서 생길 수 있는 문제를 해결할 수 있는 실마리와 이를 이용해 수행한 전자현미경 분석결과 및 효과적인 시편준비방법이 본 논문에서 언급되었다.

Keywords (주요용어): Transmission electron microscope (TEM, 투과전자현미경), Magnetic thin film hard disk (자기박막 디스크), Rocking beam thinning technique (속도가변 밀링방식), Cr-underlayer (크롬하지층), NiP substrate (NiP하지층), Sputter deposition (스퍼터 증착)

I. INTRODUCTION

Analytical electron microscopy (AEM) which is based upon the techniques of S/TEM is an essential tool for study of process-structure-property relationship of multilayer thin film disks. There is an overall agreement that the magnetic and recording properties of magnetic thin film media are strongly dependent upon the film microstructure such as grain morphology, crystallographic orientation, grain size, and physical separation.^{1,2,3,4)} However, obtaining useful information on microstructure-property

relationship requires appropriate sample preparation procedure for analytical electron microscopy. The amount of information which can be obtained from a transmission electron microscopy (TEM) is strongly dependent upon the quality of the specimen prepared. In addition, thin film disks generally show inherent variation in microstructure and thus magnetic properties from one location to another for a given disk.^{5,6)} As a result, analytical results from electron microscopy provide useful information only when the thin foil specimen is representative of the parent microstructure of whole sample. This fact can be easily overlooked in microstructure characterization of magnetic thin film media. For example, magnetron in-line sputter deposited thin film

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접수일자 : 1995년 1월 7일

심사완료 : 1995년 4월 10일

disks commonly show non-uniform magnetic anisotropy, resulting in the dispersion of magnetic properties^{7,8)}.

The determination of local composition using nano-probe X-ray chemical analysis provides a crucial clue for role of elemental segregation of non-magnetic species to media noise. Therefore, it is very important to prepare clean and artifact-free specimen from the exact location to be examined. The main purpose of this study is to investigate how improper TEM sample preparation leads to erroneous results, and how these problems can be overcome. The guideline and a road-map on the preparation of plane-view and cross-sectional TEM samples from these complex structures are described in the article. The microstructural characterization to examine the origin of the dependence of magnetic properties, and the elemental segregation using high resolution TEM and the nanoprobe X-ray chemical analysis were carried at different locations of a prototype high density disk as examples.

II. MATERIALS AND METHODS

Thin film disk possesses a complex composite structure that consists of a couple of metallic layers which are Cr-underlayer and Co-based alloy ($\text{Co}_{75}\text{Pt}_{12}\text{Cr}_{13}$; $H_c = 1730\sim 1805$ Oe, $S^* = 0.89\sim 0.91$), covered with a protective carbon overcoat. These are sputter deposited on a hard layer of NiP substrate over an Al-alloy disc. Figure 1 shows a cross-sectional schematic drawing of a hard disk sample consisting of six different layers.

II.1 Fabrication of magnetic thin film disks used for this study

For the study of cross-sectional TEM sample preparation, Co-based alloy (CoPtCr) thin films (85Å thick) used in high density longitudinal recording media were deposited on Cr-underlayer (1300Å) by DC magnetron sputtering equipped with a loadlock. The sputtering

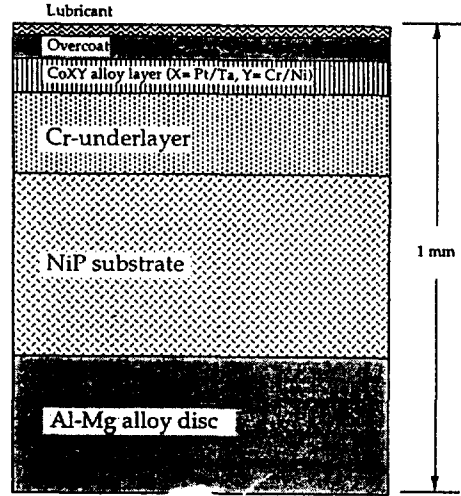


Fig. 1. A cross-sectional schematic drawing of a magnetic thin film hard disk showing the various layers.

conditions used for thin film deposition are summarized in Table 1. A prototype high density Co-alloy/Cr thin film disk was chosen for plane-view TEM sample preparation and high resolution lattice imaging.

Table 1. The sputtering conditions used for Cr-underlayer and Co-alloy thin film deposition on the textured NiP substrate.

Parameters	Conditions
Substrate temperature	190 °C
Background pressure	5×10^{-7} torr
Ar-gas pressure	10 mTorr for Cr 8 mTorr for Co-alloy
Sputtering power	0.4 KW for Cr 1.0 KW for Co-alloy

II.2 Preparation of plane-view TEM thin foil specimens

(1) Plasma-ashing, initial polishing, and disc cutting

The thin film disks were first oxygen plasma-ashed to remove any overcoat layers such as sputter deposited amorphous carbon. The plasma ashing was done at a radio

frequency (RF) of 200 watt under the oxygen gas pressure of 30 mTorr for about 10 minutes. The magnetic disk samples were then cut out from the location to be examined. For plane-view TEM sample preparation, the Al-Mg alloy substrate was partially removed by mechanical polishing with a Buehler petrographic slider. The final thickness after mechanical polishing was about 100 μm . Preliminary polishing was done using 320, 400, and 600-grit SiC emery papers. TEM sample discs with 3 mm in diameter were cut out from the polished pieces using a SBT-360 abrasive slurry cutter. The disks were then polished using 6 μm , 1 μm , and 0.25 μm diamond pastes on a microcloth.

(2) Dimple grinding and Ion-beam thinning

The NiP side of 3 mm disk specimen was dimple-ground in a Gatan dimple-grinder using a 6 μm diamond slurry until thickness of central crater is about 10 μm . A mixture of 90 volume % glycerol ($\text{HOCH}_2\text{CHOH CH}_2\text{OH}$) + 10 volume % deionized water was used as a lubricant. About 5 gram (g) load was used during dimple grinding of these materials. A schematic drawing of a dimple-ground plane-view TEM specimen is shown in Figure 2. As can be seen from the Figure 2(b), it is expected that the nearest region to a perforation gives both microstructural and chemical information only from the magnetic recording layer which is a Co-alloy in this case.

The deposition effect of sputtered material flux during the ion beam thinning on specimen quality was examined since material sputtered from the specimen could be deposited on the other side of the specimen and the airlock viewing port. Over a period of time this would make it difficult to see the specimen and might affect the function of the autoterminator. To access this problem, two different sample preparation approaches were tailored. The one was covered with 3 mm circular shaped mica disc on Co-alloy thin film side, while the other sample was ion milled without protection with a mica disc. The single side of specimen was

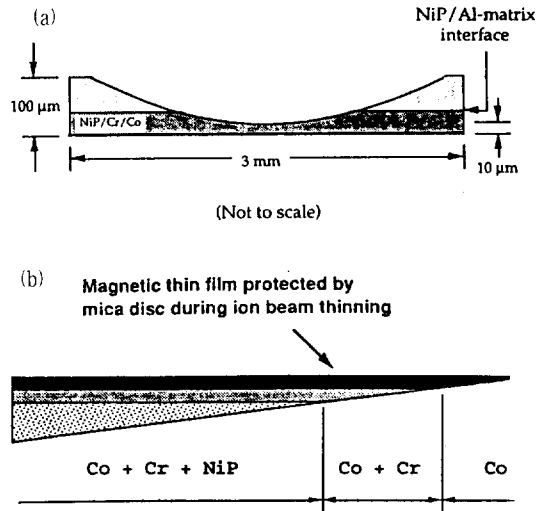


Fig. 2. Cross-sectional schematic drawing of dimple-ground plane-view TEM thin foil sample. (a) As dimple-ground, (b) After ion beam thinning

ion-milled in Gatan-600 dual ion-mill from single side with Ar^+ at 4.6 KeV at a glancing angle, 15° .

Special care was taken to cool the specimen holder with liquid nitrogen to prevent annealing or any damage of the microstructure from heating due to the ion beam radiation. A laser auto-termination device consisting of the photo-detectors and a control unit was used to sense the earliest onset of perforation and to stop milling by sensing that a preset intensity level has been exceeded.

II.3 Preparation of cross-sectional TEM thin foil specimens

(1) Plasma ashing and surface cleaning

Cross-sectional TEM specimens are crucial for investigating the microstructure of layered materials like magnetic thin film disks. The initial stage of TEM sample preparation from thin film disks consisted of oxygen plasma-ashing to remove overcoat layers as described in the previous section. The disk samples were then sectioned by a low speed diamond wafering saw (Buehler Isomet) into 4

mm x 8 mm rectangular slabs. The Al-Mg alloy substrate was completely removed by mechanical polishing with Buehler petrographic slider to leave only the CoPtCr/Cr layers on textured NiP substrate. The final thickness after mechanical polishing was about 13 μm .

Trichloroethane-based solvent was applied to degrease the surface of polished disk sample. Preliminary polishing was done using 320, 400, and 600-grit SiC emery papers on one side of surfaces. The sample was thoroughly rinsed in a water-based alkaline surface cleaner (M-Prep conditioner). This was followed by wiping dry with cotton tipped applicators. Few drops of a water-based alkaline surface cleaner (M-Prep neutralizer) was applied and gently scrubbed with a cotton-tipped applicator. Here, the purpose of surface preparation was to develop a chemically clean surface suitable for TEM sandwich composite making. Solvent degreasing was performed to remove organic contaminants and any soluble chemical residues. After thorough cleaning in acetone and isopropyl alcohol ($\text{CH}_3\text{CHOHCH}_3$), two silicon single crystal slabs of (111) orientation were glued together face to face by using the M-bond 610 adhesive which is a high-performance epoxy resin.

(2) TEM sandwich sample preparation

M-Bond 610 adhesive was prepared using the following steps. Contents of curing agent bottle was poured into an adhesive resin bottle by using the disposable plastic funnel. After tightening the brush cap, contents of this adhesive bottle was thoroughly mixed by shaking it for about 30 seconds. This freshly mixed adhesive was allowed to stand for two hours at room temperature before using. The thin specimen sheet was then glued between two 1.5 mm thick pieces of silicon single crystal wafer blocks of (111) orientation with M-bond 610 adhesive. The assembly was put in a hand screw mini-clamp, and pressed to finger tight. The applied pressure was about 30 psi (200 KN/m^2). The clamped specimen was placed into an oven at room temperature and raised to the

level of desired curing temperature at a heating rate of 5°C per minute. The composites were cured at 120°C for two hours and slowly cooled. Theloco vacuum oven (Precision Scientific Co., M19) was employed for this curing step. An optical micrograph of TEM sample showing the arrangement of cross-sectional sandwich is shown in Figure 3.

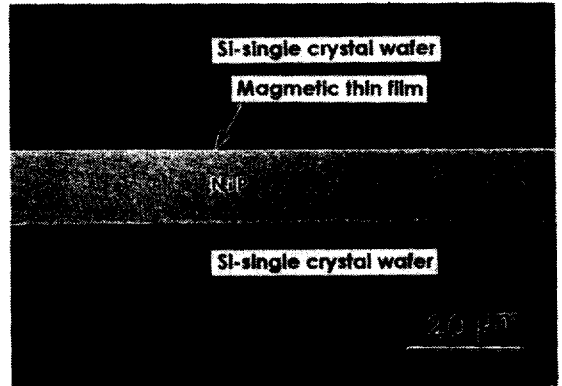


Fig. 3. An optical micrograph of TEM sample showing the arrangement of cross-sectional sandwich

(3) Slab slicing, 3mm disc cutting, and initial polishing

After cooling to room temperature, the composite was mounted on a stage glass with crystal bond and sliced with a diamond wafering saw. The slabs with the thickness of 0.5 ~ 0.8 mm were then cut out from the composite sandwich at right angle to the bond-line with a low speed diamond saw. The slices were mechanically polished parallel to the bond-line from both sides starting with 600 grit emery paper and finishing with 1 μm diamond paste to 150 μm thickness. Discs, 3 mm in diameter, were cut out from the polished slices that were centered on the magnetic film. A SBT-360 abrasive slurry cutter was used with 600 mesh size of SiC abrasive powder to cut the disks. The disks were then polished with a 6 μm diamond paste on a polishing pad, and finally a 0.25 μm diamond paste on a microcloth. Next, the disks were mounted with crystal bond so that the smoothly polished side

is face down on a polishing glass platen prior to further polishing to $100\sim 120\ \mu\text{m}$ in thickness. Finally the slices were removed from the stage glass and thoroughly cleaned in acetone.

(4) Dimple-grinding

The specimen was dimple-ground in a Gatan dimple-grinder (or South Bay Technology Inc., SBT 515 dimpler) using a $6\ \mu\text{m}$ diamond slurry with the center of the crater located at the area of interest until the silicon was about $15\ \mu\text{m}$ at the bottom of the crater. A mixture of 90 volume % glycerol and 10 volume % deionized water was used as a lubricant. The thickness of a dimpled specimen was easily established by visual inspection, since the silicon transmits red light at about $15\ \mu\text{m}$. Its color was bright red when illuminated through the lucite sample stage which is transparent. A final polish with a $0.25\ \mu\text{m}$ diamond slurry on an adhesive backed microcloth strip attached to the dimpling wheel completes the process.

(5) Ion beam thinning

Finally, the specimen was ion-milled from both sides in a Gatan-600 dual ion-mill using a liquid nitrogen cooled stage to minimize hydrocarbon contamination on the specimen. The conditions during the ion milling are summarized in Table 2. The perforated sample was further ion-milled in the low angle specimen stage with incidence angle of $3\sim 5$ degrees ($^{\circ}$) for about another 4 hours. In multilayer structure, one component may perforate first while the other layer is still electron-opaque because of the different ion milling rates. However, it was clear from the present study that the most successful approach for overcoming this problem is to use the rocking ion beam. It uses different rotating speed and angle of the specimen. For example, specimen rotates slowly when the ion beam is perpendicular to the glue-line in the sandwich sample and rapidly through the remaining sectors so that overall thinning rate is almost same each other. The use of rocking ion mill controller during this stage was also tried and resulted in excellent sandwich-type TEM thin foil specimen for examination under the

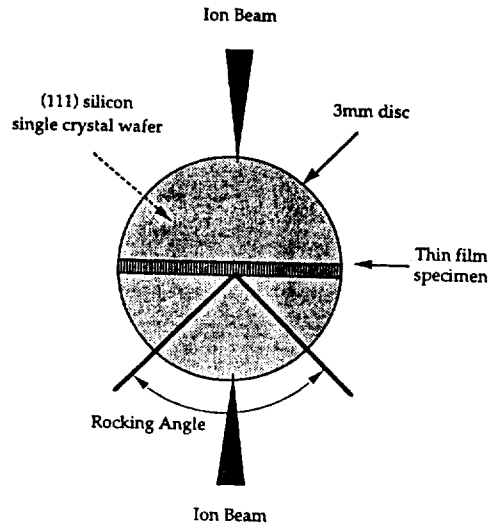


Fig. 4. A schematic diagram of the rocking motion control used for elimination of preferential ion milling axis in the cross-sectional TEM specimen preparation.

transmission electron microscopy. A schematic diagram showing the rocking motion control is given in the Figure 4. The rocking motion confines the ion beam to a narrow angle, typically around $60\sim 80$ degrees ($^{\circ}$), and effectively avoids the preferential ion milling axis compared to the conventional ion beam thinning.

Table 2. Ion milling parameters used for TEM sample preparation.

Parameters	Conditions
Accelerating voltage	4.5 ~ 5.0 KV
Gun current	0.5 mA
Specimen current	27 ~ 33 mA
Ion beam angle ($^{\circ}$)	$15^a, 4^b$

a Initial ion milling

b Low angle ion milling

For the microstructural characterization of TEM specimens prepared, TOPCON EM-002B,

and VG HB501/STEM equipped with a field emission gun (FEG) were used for high resolution lattice imaging and nano-scale X-ray chemical analysis, respectively. The nano-probe X-ray chemical analysis of solute segregation to grain boundaries in polycrystalline CoPtCr magnetic thin films was carried out by combined use of 10Å size electron microprobe in a VG HB501/STEM and Link Analytical LZ-5 windowless detector.

III. RESULTS AND DISCUSSION

Figure 5 shows an optical micrograph of an as-dimpled plane-view TEM thin foil specimen. As can be seen from the figure, a plane-view of the specimen reveals three different regions; as-abrasive cut 3 mm disc, polished Al-Mg alloy matrix, and as-dimpled region. It has been well known that ion beam thinning is a standard method for thinning magnetic thin film specimens after dimple-grinding. However, two problems quickly became apparent in the plane-view TEM specimen occurred during whole ion-milling process. First, sputtered material fluxes were heavily redeposited on the magnetic thin film side to be examined under the analytical electron microscopy. Second, this caused the high resolution imaging of thin film sample difficult. In general, redeposition can be reduced by sputtering from both directions. In plane-view TEM sample, however, one magnetic thin film side must be protected from ion-beam thinning flux. Research toward optimal TEM sample preparation techniques to minimize these problems proceeded through several iterations of ion thinning processes. It was shown from the present study that use of 3 mm disc shaped mica sheet was most effective to avoid this redeposition problem.

On the other hand, the isolation of magnetic grains to reduce the exchange interaction between neighboring grains is essential for achieving high storage densities. In general, this magnetic decoupling can be accomplished by formation of physically separated columnar

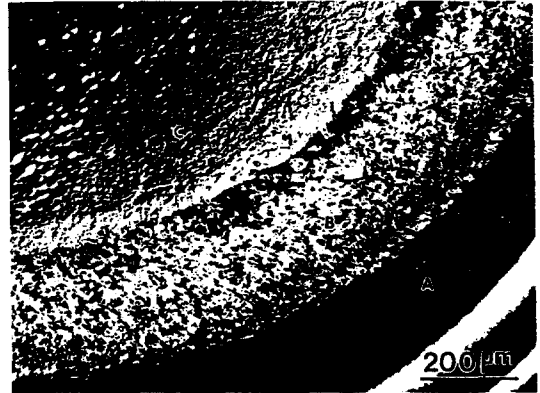


Fig. 5. An optical micrograph of an as-dimpled plane-view TEM thin foil showing three different regions. A: as-abrasive cut 3 mm disc, B: polished Al-Mg alloy matrix, C: as-dimpled region.

grains along the boundary or the elemental segregation of non-magnetic solute atoms by controlling the sputtering conditions and Cr-underlayer thickness.^{9,10,11} In order to determine the local composition of non-magnetic species (Cr and Pt in this case), a nano-probe x-ray chemical analysis was done. It was shown from the present study that the redeposition of sputtered atom flux possibly leads to erroneous results on exact composition from the local areas like grain boundary or grain interior regions. Therefore, it was turned out to be essential to protect the Co-alloy thin film side from redeposition atom flux in TEM sample preparation for analytical electron microscopy. Typical results of EDS spectra are given in elsewhere.¹¹ It was clear from those results that Cr segregates to the grain boundary in magnetron sputter deposited CoPtCr magnetic thin films, explaining dependence of magnetic media noise on thin film microstructure.

In the preparation of cross-sectional TEM specimens from magnetic thin film disks, one of the major difficulties is the large difference in ion beam thinning rate along the interface like bond/glue line. One way to avoid this preferential ion beam thinning is to use the low incidence angle sputtering with glue-line

direction shielded from the ion beams. However, this technique requires to use the special sample holder or blocks for ion beam shielding. In attempts to eliminate this preferential axis problem, an ion beam thinning method was modified to the conventional technique using a uniform sample rotation. A rocking motion control was employed and was turned out to be very effective for avoiding the

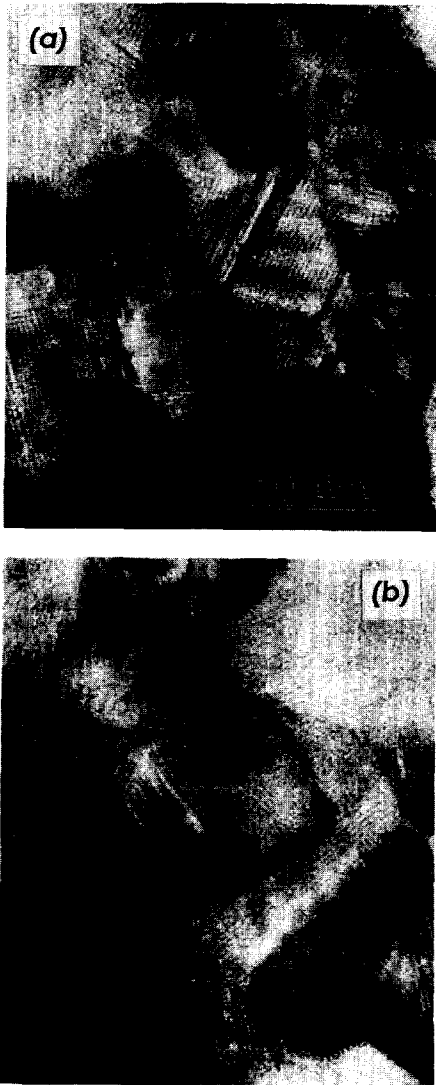


Fig. 6. Bright field TEM microstructure of thin film disk from plane-view specimens with magnetic layer protection using a 3 mm mica disc.

preferential ion milling axis in TEM sandwich specimen like magnetic thin film multilayers. Figure 7 shows a macro-view of a cross-

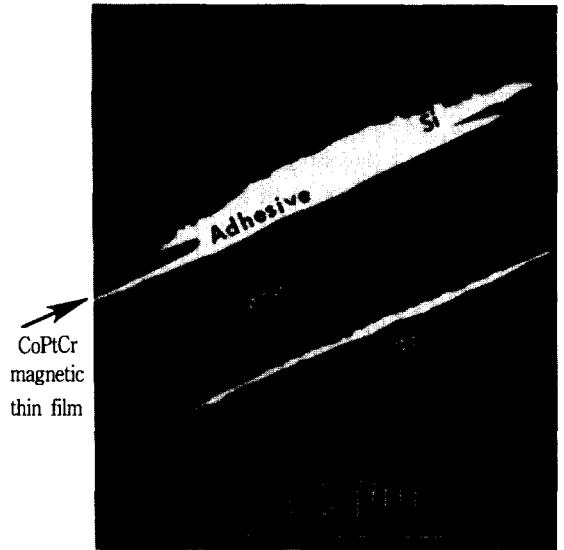


Fig. 7. Magnified view of a cross-sectional TEM thin foil showing detailed layers. The Cr-underlayer is located beneath the Co-alloy thin film.

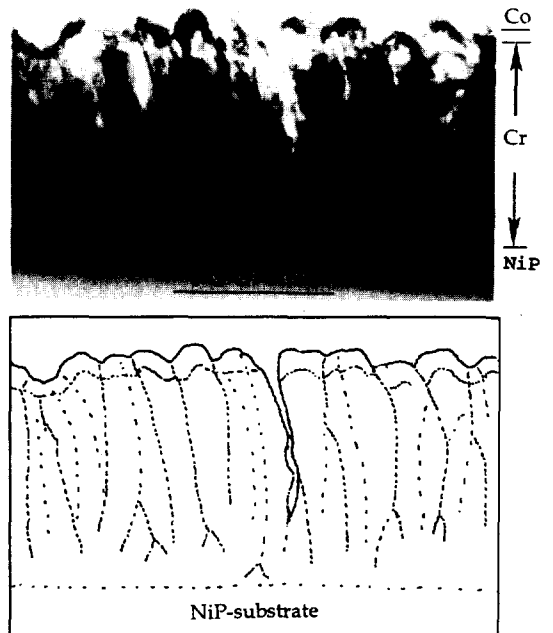


Fig. 8. Cross-sectional TEM micrograph of magnetic thin film showing the microstructure evolution during sputter deposition.

sectional TEM thin foil showing the detailed structure. As shown in Figure 8, the TEM sample preparation route described here turned out to be extremely effective to reveal the evolution of cross-sectional microstructure of delicate specimen which is a 85Å thick CoPtCr magnetic thin film on 1300Å thick Cr-underlayer. It is clear from the cross-section that Cr and Co-layers grow in the manner of columns with increase in film thickness.

IV. SUMMARY

A prototype high density $Co_{75}Pt_{12}Cr_{13}$ alloy thin film disk prepared by DC magnetron sputter deposition was used for the study of plane-view as well as cross-sectional TEM sample preparation techniques. Three principal conclusions may be drawn from the research discussed above: (1) Redeposition of sputtered material flux on the magnetic thin film side during the whole ion-milling process led to formation of serious artifact. It turned out to cause the high resolution imaging of thin film sample difficult. (2) The protection of Co-alloy thin film layer during plane-view TEM sample preparation is essential for analytical electron microscopy like nanoprobe X-ray chemical analysis for determination of local composition. It was shown from the present study that use of 3 mm circular shaped mica disc was very effective to avoid this redeposition problem. (3) One of the major difficulties arising from the large difference in ion beam thinning rate in the preparation of cross-sectional TEM specimens of magnetic thin film disks can be overcome by

using the rocking beam technique characterized by rotating slowly when the ion beam is perpendicular to the glue-line and rapidly through the remaining sectors.

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