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C.-P. LIU[1,✉]
J.-J. CHANG[2]
S.-W. CHEN[1]
H.-C. CHUNG[1]
Y.-L. WANG[3]

# Formation of pyramid-like nanostructures during cobalt film growth by magnetron sputtering

[1] Department of Materials Science and Engineering, National Cheng-Kung University, Tainan, Taiwan, R.O.C.
[2] Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, Taiwan, R.O.C.
[3] Taiwan Semiconductor Manufacturing Company, Hsinchu, Taiwan, R.O.C.

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**ABSTRACT** Cobalt pyramid-like nanostructures with sharp tips were formed on the surfaces of cobalt thin films grown by magnetron sputtering only when a negative bias was applied. There are two types of pyramids, which grew on top of a columnar grain structure directly from Si(001) substrates. The formation of pyramid-like nanostructures is only selective to a ε-Co (hcp) thin film but not a α-Co (fcc) thin film, where the basal plane is $10\bar{1}0$ with several well-defined low-energy faceted planes. When grown on Si(111) substrates, the shape of the basal plane changes to a pentagon or other polygon. The island nucleation seems to depend on adatom energy, sputtering rate and the interface stress between the Co thin film and the substrate, but growth is significantly determined by the minimum surface configuration of the structure.

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## 1 Introduction

Cobalt possesses superior electrical and magnetic properties and hence has attracted much attention to its fundamental growth and potential application [1, 2]. Especially, cobalt nanostructures might be applied in magnetic recording media or carbon nanotube (CNT) growth as the most active catalytic site [3]. Metal with a sharp tip can also be applied in field-emission flat-panel displays [4–6], where the sharpened tip results in a lower work function to give rise to a high current density. However, the pyramid-shaped tips often require an extra etching process [4–7] on cobalt films. In this paper, we find that pyramid-like nanostructures with sharp tips can be naturally formed without any post-etching process by selective growth with dc magnetron sputtering. The evolution of the pyramid-like nanostructures was systematically examined with various processing parameters and the growth mechanism was investigated. Through the study, we provide a simpler growth method to fabricate a sharp-tipped Co metal film.

## 2 Experimental details

A dc magnetron sputterer was employed to deposit Co thin films on *n*-type Si(100) and (111) substrates. The substrates were chemically cleaned before loading into the chamber. The Co target (99.95% purity) was pre-sputtered for 10 min as soon as the base pressure of $3 \times 10^{-6}$ Torr was reached using argon (99.995% purity) as the sputtering gas. During deposition, the total gas flow was maintained at 40 sccm while other deposition parameters were varied to examine the microstructure evolution of the growing Co thin films. The experiment was performed at room temperature. On the characterization side, the surface morphology, texture and phase of the evolving thin films were examined by scanning electron microscopy (SEM) (Philips XL-FEG) operated at 15 kV, X-ray diffraction (XRD) (Rigaku D-MAX-IV) with Cu $K_\alpha$ radiation and transmission electron microscopy (TEM) (Hitachi HF-2000) operated at 200 keV, respectively. The TEM cross-sectional thin foils were prepared by a focused ion beam (FIB) (FEI 205) operated at 30 kV with a gallium source to about 0.1 μm in thickness.

## 3 Results and discussion

Figure 1 shows the SEM images of the surface morphology of the as-deposited cobalt thin films with various substrate biases under the deposition distance of 6 cm and the applied power of 50 W. The pyramid-like nanostructures are found to form on the growing surfaces. It is worth noting that the pyramid-like nanostructures only occur under an appropriate negative bias range from −30 to −60 V, while they would not form under either positive bias or negative bias outside the aforementioned range. The nanostructures have well-defined shapes with a sharp tip determined by minimum surface energy. The typical base width of the pyramids increases from about 100 nm at −30 V to 250 nm at −50 V followed by a decrease to 100 nm at −60 V. No faceted nanostructures form with a substrate bias beyond this range. This certainly implies that the formation of nanostructures is related to the energy of the deposited adatoms, which is varied by the negative bias. Since the nanostructure formation is related to the energy, we examine the morphology evolution as a function of applied power from 40 to 70 W as shown in Fig. 2 for plan-view images and Fig. 3 for cross-sectional images. The biggest size of the pyramid-like nanostructures is about 250 nm and occurs at the power of 50 W, while the size distribution changes from 60–220 nm for 40 W to 20–150 nm for 70 W. With increasing applied power, the average size decreases and the density

✉ Fax: +886-6-2346290, E-mail: cpliu@mail.ncku.edu.tw

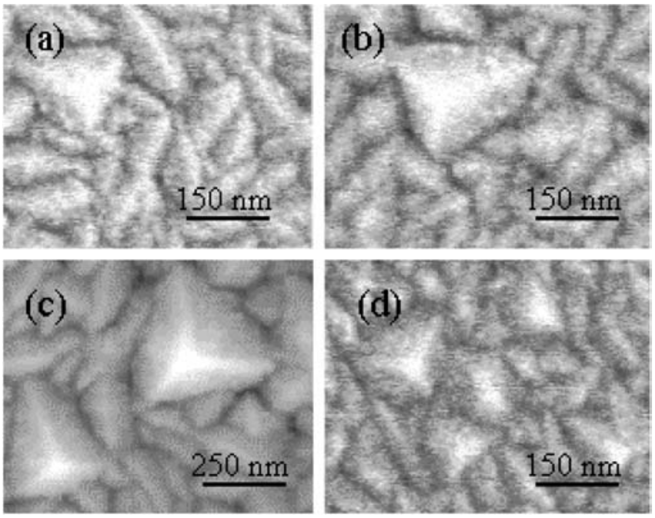


**FIGURE 1** SEM plan-view images of Co thin films as a function of substrate bias for **a** −30 V, **b** −40 V, **c** −50 V and **d** −60 V

increases, indicating that the ion-bombardment effect is more pronounced to eliminate the nanostructure growth at the high-energy regime. Both experiments by varying substrate bias and applied power reveal that both adatom kinetic energy and etching by ion bombardment determine the nanostructure formation.

Figure 4 shows a bright-field TEM cross-sectional image and a diffraction pattern of a pyramid-like nanostructure. The image shows that the nanostructure is a columnar grain with hcp phase, which grew out of the Si substrate on a basal plane of $10\bar{1}0$. The hcp structure is the same as the results from Co thin film deposition without substrate bias, where the major Co phase changes from ε-Co (hcp) to α-Co (fcc) when the deposition distance changes from 6 cm to 10 cm as evidenced from the diffraction patterns shown in Fig. 5. According to Thornton's structure-zone model [8] for sputtered metal deposits, when the $T_s/T_m$ value is between 0.1 and 0.4, where $T_s$ (K) is the substrate temperature and $T_m$ (K) is the melting point, the metal thin film will develop a typical characteristic of columnar grains for a zone $T$ microstructure. Under the lower deposition temperature condition, an adatom has insufficient mobility to diffuse a long distance laterally, so that grain growth develops into a columnar structure. Because the deposition was performed at room temperature and cobalt's melting temperature is 1495 °C, the $T_s/T_m$ value is then 0.17, which should correspond to the zone $T$ microstructure. Two types of the pyramid-like nanostructures are found on Co thin films with various faceted planes shown and assigned in Fig. 6. Based on the angles between individual faceted planes and the basal plane of $10\bar{1}0$, and the length ratios of one side

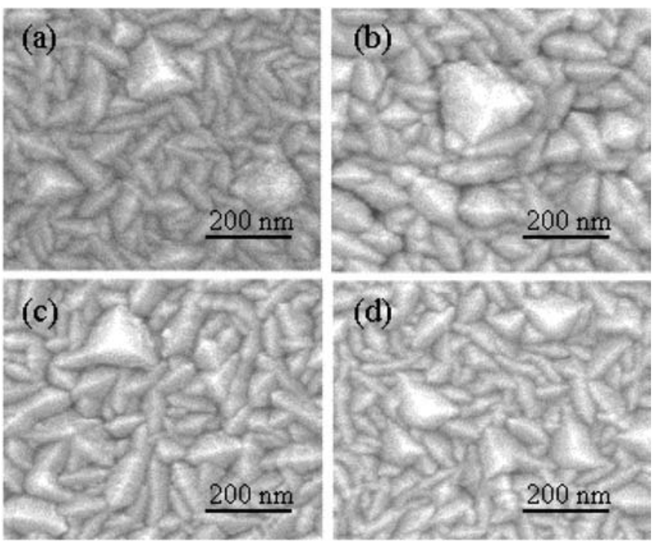


**FIGURE 2** SEM plan-view images of Co thin films as a function of applied power for **a** 40 W, **b** 50 W, **c** 60 W and **d** 70 W

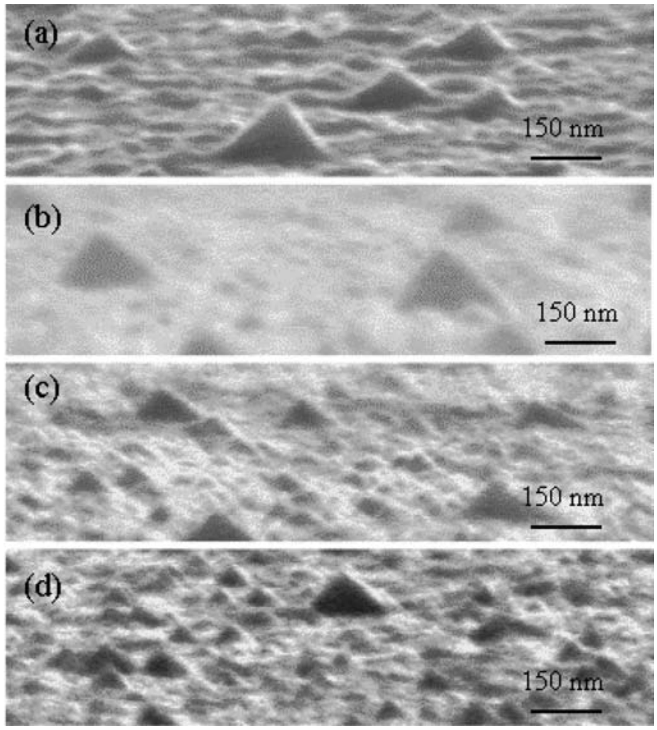


**FIGURE 3** SEM cross-sectional images of Co thin films as a function of applied power for **a** 40 W, **b** 50 W, **c** 60 W and **d** 70 W

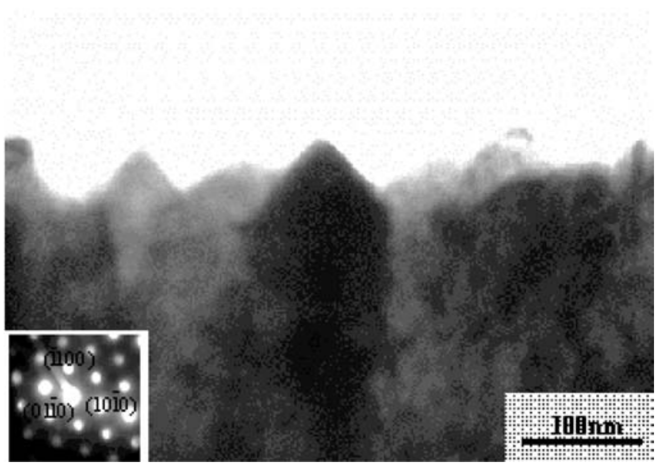


**FIGURE 4** TEM cross-sectional image and diffraction pattern of the pyramid-like nanostructures

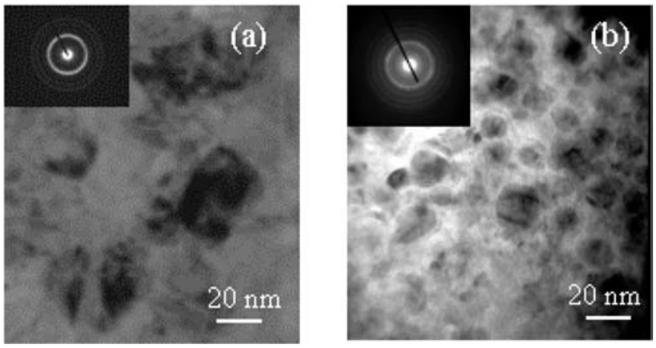


**FIGURE 5** TEM bright-field image and diffraction patterns of Co thin films deposited at **a** $d_{ts} = 6$ cm, for ε-Co (hcp) and **b** $d_{ts} = 10$ cm, for α-Co (fcc)

to the height of the basal plane triangle as sketched in Fig. 6c, we find that type I is composed of $\bar{1}013$, $02\bar{2}1$ and $2\bar{2}01$, and type II is composed of $\bar{1}013$, $01\bar{1}1$ and $1\bar{1}01$ [9]. In a hcp structure, the (0002) plane normally acts as the habit plane due to the lowest surface energy [10] and was found to be established easily when adatoms can diffuse a large distance laterally with sufficient mobility [11]. When the (0002) plane develops, faceted planes disappear. This can explain why nanostructures cannot be produced with higher applied power or substrate bias. Other evidence from texture evolution in the films by XRD is shown in Fig. 7, where the intensity ratio represents the percentage of the peak intensity from a specific plane to the intensity summation from all four major planes. Figure 7 shows that the preferred orientation is varied largely by substrate bias. The preferred orientation changes from $(10\bar{1}0)$ and $(11\bar{2}0)$ to (0002) for increasing substrate bias, where the strongest $(10\bar{1}0)$ texture occurs at $-50$ V corresponding to the highest possibility to produce a Co nanostructure, consistent with the previous results. From Fig. 7, apparently, when the bias is larger than $-75$ V, adatoms have enough mobility to form a stable (0002) plane. Conversely, when the bias is less than $-75$ V, other higher surface energy planes develop. The fact that less-stable planes dominate the texture in the as-deposited film is often seen in the zone $T$ structure and has been well explained by anisotropies in surface diffusivities and atomic shadowing [12]. Of course, the texture of a metal thin film is also influenced by deposition method, nature of the

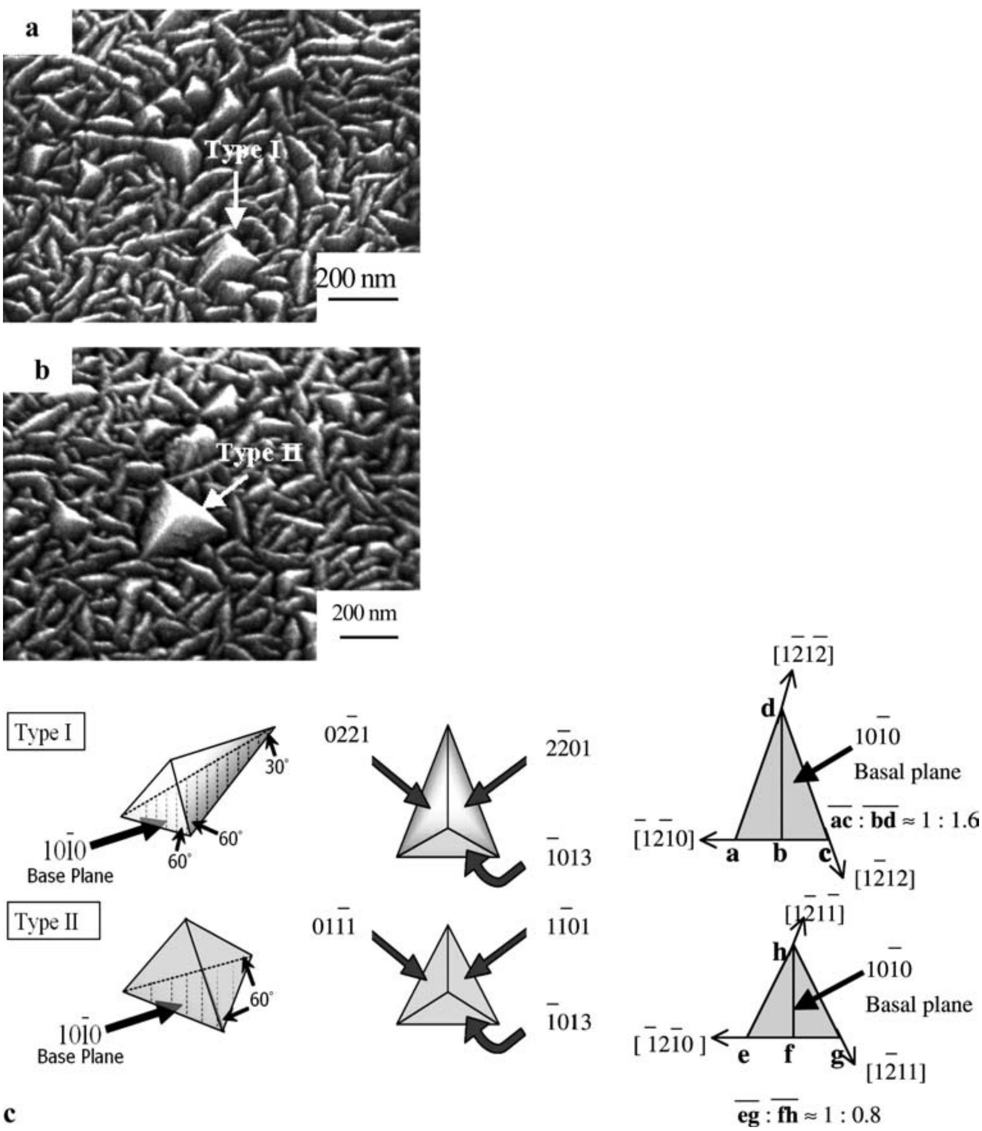


**FIGURE 6** SEM plan-view images showing faceted planes of the pyramid-like nanostructures on Co thin films for **a** type I and **b** type II; **c** schematic diagram of two types of nanostructures with detailed indices assigned for the faceted planes and edge directions

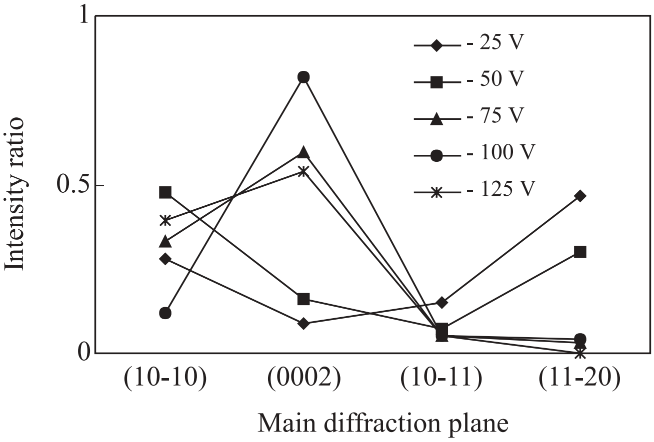


**FIGURE 7** XRD diffraction intensity ratio for four main different planes as a function of substrate bias for a fixed applied power of 50 W

substrate, energetic ion bombardment and geometrical confinement by surface features [13].

So far, we have discussed the conditions for Co pyramid-like nanostructure formation but why can a columnar grain form a pyramid-like island on top? The experimental results in that the Co nanostructure would not form under zero or smaller negative bias even with the same applied power suggest that bias-induced ion sputtering also plays an important role in the formation. Ion sputtering has been shown to induce various surface topographies, such as cone, pit and faceting, etc [14–16]. Regarding possible mechanisms responsible for pyramid formation upon ion sputtering, enhanced local erosion rate due to defect generation has been proposed [17–19] to explain the formation of symmetrical pyramids. However, both symmetrical and asymmetrical pyramids produced simultaneously with equal concentrations from our results imply that bias-induced surface diffusion to reach a minimum surface energy configuration could be the major cause.

According to Thornton [20], when the deposition temperature is lower than $T_m/3$, intrinsic stress develops because of the low adatom mobility. Wolf and Tauber [21] have also reported that sputtered metal films deposited on Si substrates at low substrate temperatures tend to exhibit tensile stress and the stress increases with thickness. Because the pyramid-like nanostructure comes from a columnar grain structure, its grain-growth process is a type of secondary grain growth [22]. Different to bulk grain growth, stress normally plays a significant role in the secondary grain growth process. In order to understand the influence of stress in the grain growth, the surface-morphology evolution of Co thin films was examined as a function of film thickness under a deposition distance of 6 cm, an applied power of 50 W and a substrate bias of −50 V as shown in Fig. 8. Figure 8 reveals that the density of smaller-sized nanostructures decreases and that of larger-sized nanostructures increases with thickness. In the low-temperature thin film growth regime, bulk diffusion of adatoms does not occur; therefore, coarsening is slower and proceeds through grain-boundary migration [23]. As a result, for increasing film thickness, stress increases and grain growth is enhanced by grain-boundary migration, which then results in increasing nanostructure size.

We also studied the surface morphology of fcc cobalt thin films deposited using a 10-cm deposition distance (please refer to Fig. 5) with various powers from 60 to 90 W, as

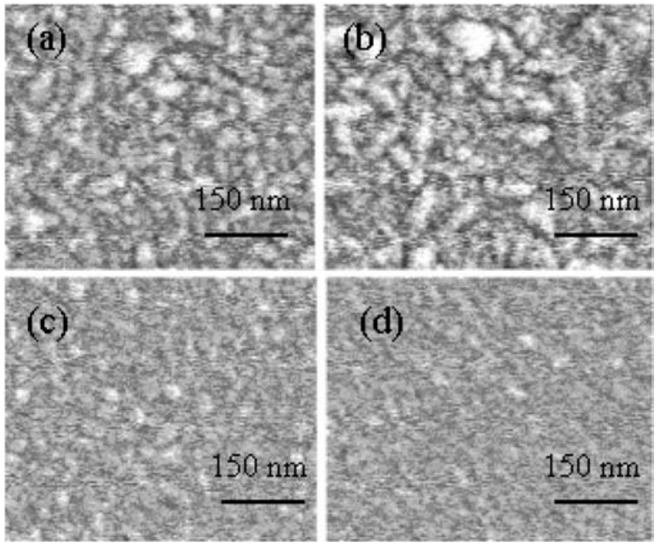


**FIGURE 9** SEM plan-view images of Co thin films deposited as a function of applied power for **a** 60 W, **b** 70 W, **c** 80 W and **d** 90 W at the deposition distance of 10 cm

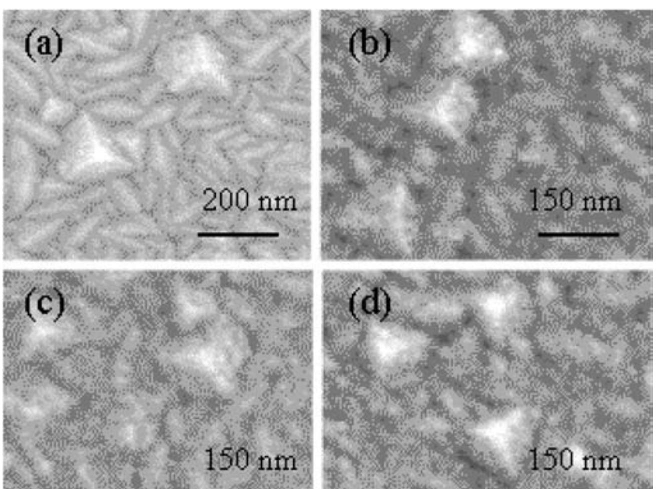


**FIGURE 8** SEM plan-view images of Co thin films as a function of thickness for **a** 1260 nm, **b** 1080 nm, **c** 900 nm and **d** 720 nm

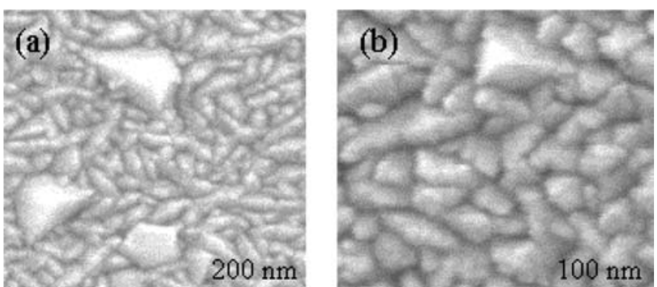


**FIGURE 10** SEM plan-view images of Co thin films deposited on Si(111) substrates, as a function of applied power for **a** 75 W and **b** 125 W

shown in Fig. 9. Surprisingly, no nanostructures are formed on the surface for all conditions and the surface becomes smooth with increasing applied power. This demonstrates that the pyramid-like nanostructure can only be formed when the cobalt thin film is hcp phase.

In order to visualize the substrate effect, cobalt was also deposited on Si(111) substrates using applied powers of 75 and 125 W, as shown in Fig. 10. The results show that the shape of the nanostructures becomes more complicated, where pyramid-like nanostructures with pentagonal or various other polygonal bases are observed. The nanostructures disappear when the ion bombardment becomes more serious at higher applied power, analogous to the case in the Si(001) substrate. These results suggest that substrate type and orientation are also significant factors for the pyramid-like nanostructure formation, probably through lattice mismatch.

## 4 Conclusion

During cobalt thin film deposition by dc magnetron sputtering, pyramid-like nanostructures were found to form on top of columnar grains only when the cobalt is hcp phase. There are two types of faceted nanostructures on Si(001) substrates, where type I is composed of $\bar{1}013$, $2\bar{2}01$ and $02\bar{2}1$ and type II is composed of $\bar{1}013$, $01\bar{1}1$ and $1\bar{1}01$ planes, with the basal plane of $10\bar{1}0$. When the basal plane changes to (0002) by varying applied power or substrate bias, these nanostructures disappear. These nanostructures would become more complicated but still faceted shapes with Si(111) substrates due to lattice mismatch. Therefore, their nucleation is enhanced by a complex function of strain, adatom energy and ion sputtering and growth is significantly determined by the minimum surface configuration of the structure.

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