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Growing sixfold symmetric osmium (Os) epitaxial films with suitable buffer layers was developed. Using a Cu buffer layer, the lattice mismatch between Os (0002) and Si (100) was significantly reduced from >30% to ~7% to grow Os films with twin relationships and weak sixfold symmetries. On the other hand, the Cu/Au buffer layer was selected to form a fcc (111) surface mesh on H–Si (111)-1×1, and therefore sixfold symmetric Os films were grown due to the lower lattice mismatch. Such growth properties may be applied in the high density magnetic random access memory manufacturing processes to connect the magnetic tunnel junction growth and Cu metal line directly. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711658]

The nonvolatile memory, magnetic random access memory (MRAM), has attracted much attention due to its high speed, high density, and radiation-resistive properties. For high density product manufacturing, it is required to combine the magnetic tunnel junction (MTJ), which is the basic cell unit of MRAM, and ultralarge scale integration (ULSI) processes. Some of the factors affecting the whole performances of MTJ are the crystallinity of the memory cell and the thermal diffusion issues. Many kinds of seed layers were used for growing a memory cell with crystalline structure on Cu to simulate the actual case during manufacturing. However, the high temperature process will cause thermal diffusion of Cu, and the MTJ will get worse once that occurred.[1] Very few epitaxial seed layers grown on Cu metal line were studied for growing crystalline magnetic films. Recently, pure osmium (Os) film was suggested to be a good glue layer and a barrier layer for Cu interconnections in Damascene processes.[2,3] Our recent work[4] showed that Os is a good buffer effort on enhancement of the magnetic property of magnetic films on SiO_2. In this letter, the growth of epitaxial Os (0002) films on Cu with sixfold symmetry was systematically studied.

Samples with the structure of Os (30)/Cu (30)/(seed layer, Au)/Si were deposited by physical vapor deposition method, where the number in parentheses are in nanometer. The Os and Cu were grown by standard magnetron sputtering, and Au was deposited by e-beam evaporation. Before deposition, all Si wafers were first cleaned by degreasing and dipping into 10% HF solution to form a hydrogen-terminated surface (H–Si). The Os and Cu were grown on substrates in sequence at the pressure of 5 mTorr pure Ar gas without breaking the vacuum. No external heating was applied to the substrates during film growth. On the other hand, the Au seed layer was deposited first when the H–Si (111) was used. Then, the deposition conditions of the following Os and Cu were as described above. The film structures were analyzed by a standard x-ray diffractometer (XRD) with a Cu $K\alpha$ source. To verify the in-plane orientation and the epitaxial relationships between layers, asymmetric in-plane XRD φ scans were carried out. The microstructure images were obtained by transmission electron microscopy (TEM).

Based on the metal-metal epitaxy on silicon (MMES) technique,[5] the Cu grown on H–Si (100) showed high (002) orientation.[6] As shown in Fig. 1(a), the XRD pattern of a 30 nm Os film growing on a 30 nm Cu (002) buffer layer on H–Si (100) showed a distinguishable Os (0002) peak and a weak Cu (002) at 41.69° and 50.43°, respectively. The intensity of the Os (0002) peak was higher than that of the Os ($10\underline{1}1$), when the thickness of the Cu layer is thicker than 10 nm. As the Os thickness increased, the intensity of the Os (0002) peak rose sharply and this indicated that the Os growth was highly textured. The XRD φ scan of the Os film on the Cu (002)/Si (100) is shown in the inset of Fig. 1(a). Four weak Cu {111} peaks implied that the Cu had fourfold symmetry. Furthermore, 12 Os $\{10\underline{1}1\}$ peaks separated by 30° were also observed, and this also indicated that the Os was a highly textured film. This special 12-fold symmetric diffraction result implied that the in-plane orientation of the Os was not totally random. Lattice constants for Os (hexagonal close-packed structure, hcp) and Si (diamond structure) are 2.74 and 5.43 Å, respectively. Not only the atomic arrangement of the H–Si (100) surface mesh is much different from that of Os (0002), but also the minimum lattice mismatch between Os and H–Si (100) is near 30% (with a 45° rotation of the Os (0002) plane around Si [001]). Thus, Os cannot grow as an oriented film directly on H–Si (100), and this can be further proven by the observation of two weak diffraction peaks, Os ($10\underline{1}1$) and Os (0002). Cu with a

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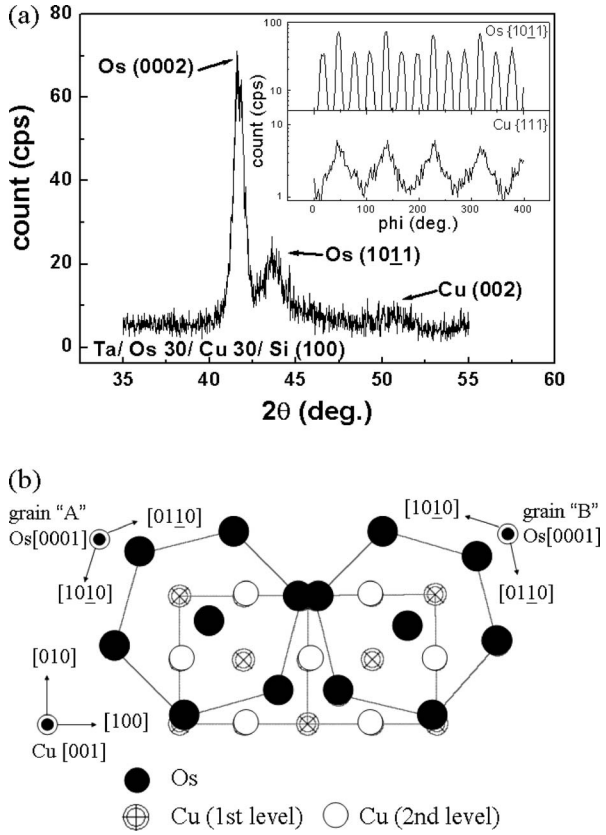

FIG. 1. (a) XRD pattern of 30 nm Os grown on Cu (002)/Si (100) showing clear Os (0002) peak. The inset panel of the figure is the XRD φ scan results of Os/Cu. A four-fold symmetric diffraction pattern of Cu {111} and a 12-fold symmetric diffraction pattern of Os {10$\bar{1}$1} were observed. (b) Illustration of the relationships between Os (0002) and Cu (002).

lattice constant of 3.62 Å can reduce the lattice mismatch to 5.5% by a 45° rotation of the Cu (002) plane around Si [001], and thus Cu can grow with a weak fourfold symmetry on H–Si (100). The lattice mismatch for Os–Cu was only 7.2% when there is a 45° rotation of the Os (0002) plane around its [0002] axis during film growth. This well-improved lattice mismatch allowed the Os to be grown as a highly textured film along the Os [0002] orientation, which is perpendicular to the substrate surface. Therefore, Cu played an important role in connecting the Os growth and Si substrate, and also the surface mesh can be changed from the fourfold symmetric structure [Cu (002)] to the sixfold symmetric structure [Os (0002)]. According to the θ-2θ scan and the φ scan results, the orientation relationships between the Cu layer and the Os layer can be determined, as illustrated in Fig. 1(b). Two sets of (0002) epitaxial grain (marked as "A" and "B" grains) rotated by 90° with respect to each other along the [0002] direction were formed in the Os layer. The relationships are as follows: Cu(002)‖Os(0002), Cu[1$\bar{1}$0]‖Os[11$\bar{2}$0], and Cu[110]‖Os[2$\bar{1}$10] in A grain and Cu(002)‖Os(0002), Cu[$\bar{1}$10]‖Os[11$\bar{2}$0], and Cu[1$\bar{1}$0]‖Os [12$\bar{3}$0] in B grain. Therefore, such an Os film showed a 12-fold in-plane symmetry from the twin relationship of the different sixfold symmetric grains. Similar structures were found in the Pd film on MgO (001) (Ref. 7) and the Au on Cu (002).[8]

The lattice mismatch could influence the Os epitaxial film growth. Since the H–Si (111) surface [H–Si (111)-1 × 1] with the (1 × 1) terminated surface has a much lower

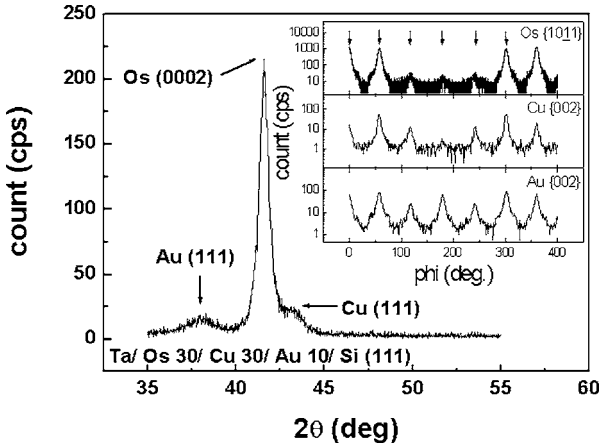

FIG. 2. (Color online) XRD pattern of Os with Cu/Au buffer layer on Si (111) and the XRD φ scan results (inset) indicating that the Os film is a good six-fold symmetric [Os (0002)] structure.

surface energy,[9] the metal which grows epitaxially on it must have the same atomic arrangement, i.e., the face-center-cubic (fcc) (111) or the hcp (0002) planes, to restrain the surface energy. However, putting Os directly on H–Si(111)-1 × 1 only showed two weak diffraction peaks, representing the Os (0002) and the Os (10$\bar{1}$1) respectively, and this is due to large mismatch (>30%) and large Os (0002) surface energy (4.57 J/m^2).[10] Thus, a buffer layer is needed to reduce the lattice mismatch and the surface energy. The body-center-cubic (bcc)-type metal cannot be a candidate because there was no bcc transition metal reported to grow epitaxially on H–Si (111)-1 × 1 due to the different atomic arrangement and the huge lattice mismatch. Hence, only the fcc or hcp metal is a suitable buffer layer for growing the Os (0002) on the H–Si (111)-1 × 1. A geometric model of the coincidence-site lattice[9] of Ag on the H–Si (111) surface suggested that the epitaxial growth occurred when it met the condition $4a_X = 3a_{Si}$. Although the lattice mismatch of Cu/H–Si (111) calculated from the coincidence-site lattice model is about 10%, the lack of an intermixed Cu silicide region at the initial Cu growth state made it hard to form a thin fcc (111) Cu layer on H–Si (111)-1 × 1.[11] Thus, the Os on such Cu/H–Si (111) surface showed neither a strong Os (0002) orientation nor an in-plane symmetry. Under these conditions, Au was selected to be the proper seed layer to grow the Cu film epitaxially due to the low lattice mismatch between Au/H–Si (111) and Cu/Au (0.1% and ~10%, respectively) In addition, the epitaxial growth properties of Au on the H–Si (111)-1 × 1 (Ref. 12) make it an appropriate selection.

Figure 2 is the XRD pattern of the 30 nm Os film grown on a 30 nm Cu (111) and a 10 nm Au (111) on H–Si (111)-1 × 1. The Os (0002) peak and the Au (111) peak were observed clearly at 41.69° and 38.18°, respectively. At the bottom of the Os (0002) peak, a broad shoulder of Cu (111) was found. Furthermore, the XRD φ scan results (as shown in the inset of Fig. 2) proved the epitaxial growth of Os once again. The six peaks from Os {10$\bar{1}$1}, Cu {002}, and Au {002} implied that these films were with a sixfold symmetric Os [hcp (0002)] and a threefold symmetric Cu/Au [fcc (111)] structure. The lower peak intensity of Os (0002) came from a slightly larger lattice mismatch between Cu/Au, and this made the Cu surface slightly more random than that of Au/H–Si (111)-1 × 1. Even so, the epitaxial quality of this Os on H–Si (111) was still better than that on H–Si (100).

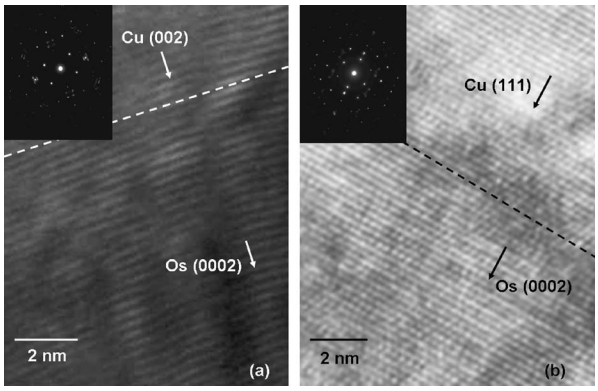

FIG. 3. High magnification TEM cross-sectional images of (a) the Os (0002)/Cu (002) interface and (b) the Os (0002)/Cu (111) interface. The growth direction is indicated by arrows. The insets of both figures are the TEM electron diffraction pattern of the Os/Cu interface.

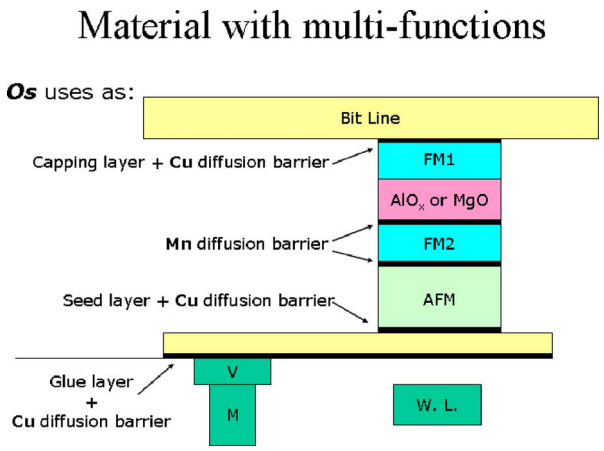

FIG. 4. (Color online) Illustration of uses of the multifunction Os that has the potential to be applied in the ULSI MTJ processes.

The comparison between the insets of Figs. 1(a) and 2 shows that the intensities of the Os $\{10\underline{1}1\}$ on Cu/Au/H–Si (111) were ten times larger than that on Cu/H–Si (100). Thus, the Cu (111) surface mesh is more suitable for growing Os (0002). Besides that, the thickness of Au can affect the Os growth. Even though the Au was as thin as 2 nm, the Cu was still able to form a fcc (111) surface. Au was accounted for the formation of long range epitaxy of Cu film, and thus the epitaxy Os (0002) film.

Figure 3 shows the high magnification cross-sectional TEM images of (a) the Os (0002)/Cu (002) and (b) the Os (0002)/Cu (111) interfaces. The insets of Figs. 3(a) and 3(b) identify the TEM electron diffraction pattern of the Os/Cu interface on both substrates. As seen from Fig. 3(a), the TEM cross-sectional image of the film showed layer by layer structure at the Os (0002)/Cu (002) interface, and the white arrows indicated the growth directions. The electron diffraction pattern with some rings also implied that this film was not totally epitaxially grown. On the other hand, the crystal growth of the Os (0002) on Cu (111) is observed on the Au/H–Si (111)-1×1. The atomic layers were grown continuously even though the Os film was as thin as 30 nm. The clear spots in the electron diffraction pattern were distinguished and they indicated that it was with epitaxial quality.

In addition, some properties of Os are highlighted once more and listed as follows: (1) the wetting angle is low and the adhesive energy is large for Cu;[2] (2) the melting temperature, electrical resistivity, and thermal conductivity are all better than those of Ta, which is the well used barrier layer in present Damascene trench;[3] and (3) Os can stop Mn diffusion[13] and enhance the CoFe/IrMn fcc (111) crystallinity on Cu/H–Si (100).[14] Considering the results of this study and the characteristics mentioned, Os has a huge potential to be applied in the ULSI MRAM processes. Since the (111) oriented Cu film can be grown in the Cu metallization process,[15] Os can act as a multifunction material, as presented in Fig. 4. Os was proposed to be the underlayer for Cu metal line or glue and barrier layers for Cu interconnect.[2,3] Os can also be posited in the MTJ/Cu metal line interface to reduce the Cu interdiffusion into the MTJ cell and simultaneously enhance the fcc (111) crystallinity of the magnetic films in MTJ. Thus, Os does have high application potential and will play an important role in integrating the ULSI and MTJ processes.

In summary, a method to grow Os films epitaxially with sixfold symmetry by using suitable buffer layers was developed; this provided a controllable way to grow high crystal quality Os films. By using the Cu buffer layer, the lattice mismatch was reduced significantly from >30% to ~7%. Thus, the highly textured Os growing on the Cu (002)/H–Si (100) with a twin relationship showed a special 12-fold in-plane symmetric diffraction result. On the other hand, for epitaxially growing better sixfold symmetric Os films, the Cu/Au buffer layers were selected to form a fcc (111) surface mesh on H–Si (111)-1×1, while a 10 nm Au seed layer was used to decrease substantially the lattice mismatch between Cu and H–Si (111). Substantially, with such an excellent growth technique, Os has the potential of growing high fcc (111) orientation MTJ directly on the ULSI Cu metal line.

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[1] J. Schmalhorst, H. Brückl, G. Reiss, G. Gieres, and J. Wecker, J. Appl. Phys. **91**, 6617 (2002).
[2] H. Kim, Y. Naito, T. Koseki, T. Ohba, T. Ohta, Y. Kojima, H. Sato, and Y. Shimogaki, Jpn. J. Appl. Phys., Part 1 **45**, 2497 (2006).
[3] D. Josell, C. Witt, and T. P. Moffat, Electrochem. Solid-State Lett. **9**, C41 (2006).
[4] T. Y. Peng, C. K. Lo, S. Y. Chen, and Y. D. Yao, J. Appl. Phys. **99**, 08C907 (2006).
[5] Chin-An Chang, J. Vac. Sci. Technol. A **8**, 3779 (1990).
[6] H. Jiang, T. J. Klemmer, J. A. Barnard, and E. A. Payzant, J. Vac. Sci. Technol. A **16**, 3376 (1998).
[7] H. Fornander, J. Birch, L. Hultman, L.-G. Petersson, and J.-E. Sundgren, Appl. Phys. Lett. **68**, 2636 (1996).
[8] C. H. Lai, Y. H. Wang, and R. T. Huang, Appl. Phys. Lett. **85**, 2298 (2004).
[9] B. Q. Li and J.-M. Zuo, Surf. Sci. **520**, 7 (2002).
[10] L. Vitos, A. V. Ruban, H. L. Skriver, and J. Kollar, Surf. Sci. **411**, 186 (1998).
[11] B. G. Demczyk, R. Naik, G. Auner, C. Kota, and U. Rao, J. Appl. Phys. **75**, 1956 (1994).
[12] S. Hasegawa and S. Ino, Phys. Rev. Lett. **68**, 1192 (1991).
[13] Tai-Yen Peng, C. K. Lo, San-Yuan Chen, and Y. D. Yao, J. Magn. Magn. Mater. **304**, E50 (2006).
[14] Tai-Yen Peng, C. K. Lo, San-Yuan Chen, and Y. D. Yao, IEEE Trans. Magn. **43**, 894 (2007).
[15] K. Abe, Y. Harada, M. Yoshimaru, and H. Onoda, J. Vac. Sci. Technol. B **22**, 721 (2004).