Magnetic tunnel junctions thermally stable to above 300 °C

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Magnetic tunnel junctions formed from sandwiches of magnetically hard $Co_{75}Pt_{12}Cr_{13}$ and magnetically soft $Co_{88}Pt_{12}$ ferromagnetic layers separated by thin alumina tunnel barriers are shown to be thermally stable to temperatures in excess of 300 °C. A comparison of cross-section transmission electron micrographs of an untreated sample and a similar one annealed at 350 °C indicates that the thickness of the amorphous tunnel barrier is slightly decreased after annealing. The resistance and magnetoresistance are only slightly affected by annealing at temperatures of up to ~300 °C but then decrease monotonically at higher annealing temperatures. Interaction of the alumina layer with the adjacent ferromagnetic layers is the likely cause of this decrease. © *1999 American Institute of Physics.* [S0003-6951(99)01229-2]

There has been considerable recent interest in magnetic tunnel junction (MTJ) structures.[1–4] MTJs are typically sandwiches of two ferromagnetic layers separated by a thin insulating layer through which electrons tunnel. The conductance across the sandwich depends on the relative magnetic orientations of the ferromagnetic (FM) layers, being higher when the magnetic moments are parallel. MTJs thus have potential applications as magnetic memory storage cells and as magnetic field sensors.

Two basic types of MTJs have been studied. Dating from the earliest reported work in 1975,[5] most studies[1,2,6] have involved hard-soft (HS) MTJ structures in which the magnetic moments of the two ferromagnetic layers were formed from magnetic materials with different magnetic switching fields. The magnetic moments of the two layers can then be arranged to be parallel or antiparallel for certain magnetic field ranges. In a second type of MTJ structure, of more recent interest, one of the FM layers is exchange biased or pinned by an adjacent antiferromagnetic layer so that the magnetic hysteresis moment of this layer is shifted from zero field by an offset field.[3,4] The presence of the antiferromagnetic layer makes this type of MTJ structure necessarily more complicated than simpler HS MTJs. In particular, HS MTJs may have advantages for magnetic memory applications, for which the MTJ device must be able to survive relatively high processing temperatures. In this letter, we report HS MTJ devices in which significant magnetoresistance remains even after thermal treatments to above 350 °C.

The MTJ structures were prepared by dc magnetron sputtering at room temperature (~30 °C) on (100) silicon wafers on which ~500 nm SiO_2 had been grown by wet thermal oxidation. Ten MTJ devices, each with an area of $\sim 100\times 100\,(\mu\mathrm{m})^2$, were patterned by using metal shadow masks. MTJ devices were prepared on as many as twenty one-inch-diameter Si wafers in a single pumpdown of the vacuum system which had a base pressure below 1×10^{-9} Torr. The films were deposited at a rate of 0.1–0.2 nm/s in an atmosphere of 3 mTorr argon. The magnetic properties of the MTJs were studied using SQUID magnetometry, and their transport properties were measured using conventional four-probe dc current techniques. Cross-sectional samples were prepared for electron microscopy observation using standard techniques of mechanical polishing, dimpling, and argon-ion milling at liquid nitrogen temperature. Electron micrographs were recorded with a JEM-4000EX high-resolution electron microscope operated at 400 keV.

The thermal stability of the MTJ films was studied in a specially constructed high vacuum annealing furnace with a base pressure of $\sim 10^{-8}$ Torr. The sample was placed on a thin copper block which itself was directly in contact with a pyrolytic graphite heater encapsulated in boron nitride. All ten junctions on each silicon wafer could be electrically accessed by means of 26 spring-loaded contact probes designed to withstand temperatures in excess of 400 °C. The contact probes were attached to an assembly that could be raised and lowered by an external stepper motor. Thus the probes could be removed, if desired, from the surface of the wafer during thermal treatments. An external electromagnet on a motorized rotatable table was used to apply magnetic fields (±10 kOe) in the plane of the wafer. The resistance versus field curves of a subset of junctions on one wafer were measured at close to room temperature (typically 50 °C) following a sequence of thermal annealing treatments at temperatures up to 430 °C. The experiment was completely automated.

In these studies, the lower FM electrode was selected as the magnetically harder layer since underlayers can often be useful as a means to promote the growth of appropriate high anisotropy alloys. This is not possible with the upper FM electrode since this layer must be grown directly on the tunnel barrier. Useful FM alloys with high magnetic anisotropy include, for example, the well-known family of *hcp* Co–Pt–Cr and related alloys, which are used as thin film magnetic media for high density magnetic recording applications.[7,8] A variety of such alloys was explored, although only results for $Co_{75}Pt_{12}Cr_{13}$ are presented here.

A lower FM electrode of the form 25 nm $Cr_{80}V_{20}$/15 nm $Co_{75}Pt_{12}Cr_{13}$ was formed by depositing through a first

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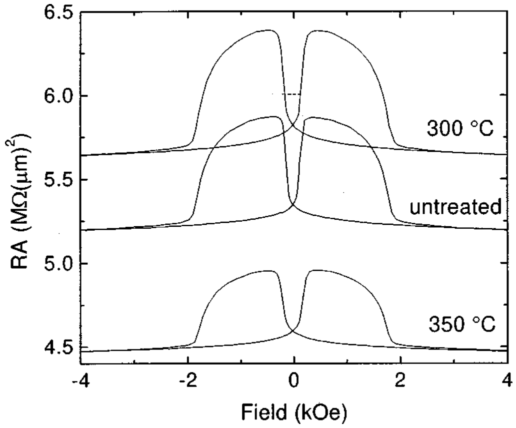

FIG. 1. Resistance vs field curves, measured at 50 °C, for a hard-soft MTJ structure of the form Si/SiO/25 nm $Cr_{80}V_{20}$/15 nm $Co_{75}Pt_{12}Cr_{13}$/1.4 nm Al plasma oxidized for 240 s in 100 mTorr O_2/15 nm $Co_{88}Pt_{12}$/20 nm Al. The curves correspond to (a) the as-deposited film, and (b) and (c), after a sequence of 65 min anneals at a succession of temperatures increasing from 50 to 300 °C and from 50 to 350 °C, respectively.

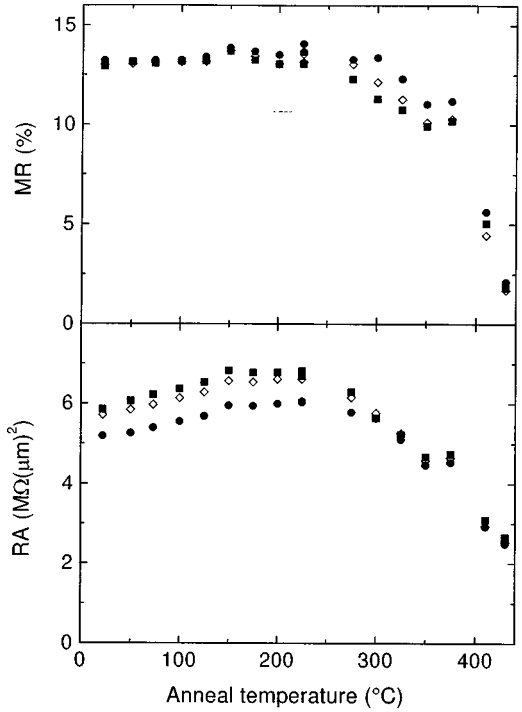

FIG. 2. (a) Saturation magnetoresistance and (b) specific resistance for the MTJ structure shown in Fig. 1, measured at 50 °C, vs final anneal temperature, after a sequence of progressive 65 min anneals at increasing temperatures from 50 to 430 °C. Data for three nominally identical junctions prepared on a single silicon wafer are shown.

metal contact mask. The tunnel barrier was subsequently formed by depositing a thin metallic layer of aluminum through a second mask. After removal of this mask the Al was plasma oxidized by placing the substrate in an oxygen plasma confined within cylindrical electrodes. Finally, the top FM electrode, of the form 15 nm Co/20 nm Al or 15 nm $Co_{88}Pt_{12}$/20 nm Al was deposited through a third shadow mask. The Cr–V alloy underlayer in the lower FM electrode was intended as a seed layer to promote growth of the *hcp* Co–Pt–Cr alloy with its *c* axis (and magnetic easy axis) oriented in the plane of the film. The coercivity of the Co–Pt–Cr film was ~2000 Oe at room temperature, whereas the $Co_{88}Pt_{12}$ layer had a much lower coercivity of ~100 Oe.

The resistance versus field curve of an untreated sample is shown in Fig. 1(a). This sample was grown with an Al layer of 1.4 nm thickness which was plasma oxidized in 100 mTorr oxygen for 4 min. The MTJ displays increased resistance for fields at which the moment of the $Co_{75}Pt_{12}Cr_{13}$ layer is approximately antiparallel to that of the $Co_{88}Pt_{12}$ layer. The magnetoresistance of the as-deposited MTJ is approximately 13%. Since the remanent magnetization of the $Co_{75}Pt_{12}Cr_{13}$ layer, as inferred from SQUID magnetometry measurements, is about 70% of its saturation magnetization, still larger MR values should be possible with higher remanent magnetization values. However, it is known to be difficult to prepare CoPtCr thin films with large coercive fields and very high remanent magnetization.[9] Interestingly, the insertion of thin Co layers at the interface between the $Co_{75}Pt_{12}Cr_{13}$ layer and the tunnel barrier in otherwise similar MTJ structures resulted in very little change of the MR even though the magnetization of the $Co_{75}Pt_{12}Cr_{13}$ layer was measured to be only about 43% of that of pure Co (~600 vs ~1400 emu/cc, respectively). Similarly, the MTJ magnetoresistance was only slightly affected by using $Co_{100-x}Pt_x$ ($x \leqslant 25\%$) soft layers instead of pure Co soft layers. This is perhaps a surprising result since it is generally believed that the spin polarization of electrons tunneling from a ferromagnetic film across an alumina tunnel barrier increases with the magnetization of the ferromagnetic film.[10] One intriguing possibility is that the electrons preferentially tunnel to and from the Co in the CoPtCr and CoPt layers. One anticipates that the tunneling current will depend, in detail, on the nature of both the FM material and the tunnel barrier and, in particular, on the detailed electronic structure of the FM/barrier interface. Thus perhaps the tunneling may be enhanced for electrons with significant Co character.

Figures 1(b) and (c) compare resistance versus field curves of the same sample after sequential ~65 min long anneals at a series of progressively higher temperatures, increasing from 50 °C, in 25 °C increments, to 300 and 350 °C, respectively. The shape of the resistance curve is hardly affected by the thermal treatments indicating that the magnetic properties of the hard and soft layers have not changed substantially. However, both the resistance and the MR of the sample do actually change. Figure 2 shows the variation of the MR and the specific resistance of the same sample, measured at 50 °C, plotted as a function of the maximum annealing temperature, for annealing temperatures of up to 430 °C. Results are shown for three junctions on the same wafer, but similar results were obtained for other samples. Typically, as shown in Fig. 2, the resistance and the MR of the devices initially increase slightly for lower temperature annealing treatments up to about 200–250 °C. For higher temperature anneals, both the MR and the resistance decrease monotonically, although the MR decreases at a more rapid rate. It is noteworthy that MR values of ~10% are still obtained after annealing to ~350 °C.

The structure of related samples was explored using cross-section transmission electron microscopy (XTEM), before and after similar annealing treatments in a conventional vacuum furnace. The samples were tilted to the (110) orientation of the Si substrate so that the metal layers were oriented edge-on to the electron beam direction. Representative micrographs of an MTJ, nominally identical to that displayed

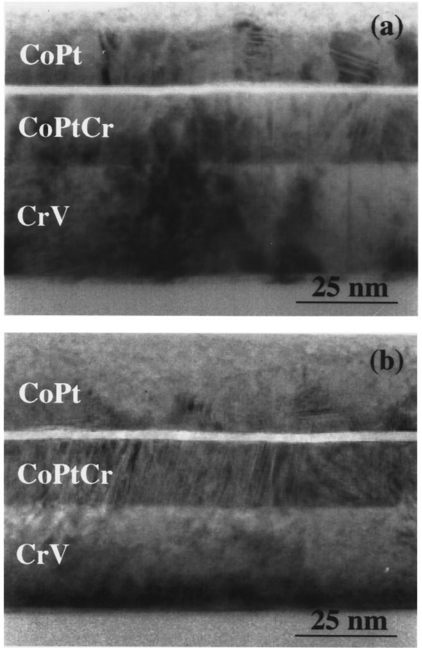

FIG. 3. Low magnification electron micrographs showing the entire cross section of an MTJ of the form Si/SiO/25 nm $Cr_{80}V_{20}$/15 nm $Co_{75}Pt_{12}Cr_{13}$/1.4 nm Al plasma oxidized for 240 s in 100 mTorr O_2/15 nm $Co_{88}Pt_{12}$/20 nm Al, (a) before annealing and (b) after annealing at 350 °C. (a) was recorded with a small objective aperture to enhance diffraction contrast.

in Figs. 1 and 2, are shown in Figs. 3(a) and 3(b). The first is an as-deposited sample and the second is one that had been annealed at 350 °C. Note that these micrographs originate from different pieces of the same wafer. This pair of images demonstrates the polycrystalline and columnar nature of the metal layers, especially (a) which was recorded with a small objective aperture to deliberately enhance diffraction contrast effects. The strong dark contrast thus corresponds to regions where metal crystallites are oriented close to diffracting conditions. A slight waviness is visible in the alumina barriers, which are the roughly horizontal lines of strong white contrast in each image. Some waviness must be expected because the layers are conformal to the sputtered CoPtCr underlayers, which have some inherent roughness. There is no evidence in any of the recorded micrographs for bridging between the metal layers on each side of the barrier.

The pair of high-resolution images in Fig. 4 shows the region of the alumina barrier for the sample as-grown (a), and after annealing at 350 °C (b). In both cases, lattice fringes from oriented crystallites are visible in parts of the FM layers on either side of the central alumina layer. The barrier itself, which is again readily identified as the central region of lighter contrast, shows a random appearance corresponding to its amorphous structure. From several micrographs it was concluded that the alumina layers had remained continuous and relatively flat after annealing. However, measurements of the layer widths indicated that the mean barrier thickness had decreased slightly by about 10% from about 2.7 nm for the as-grown sample to about 2.5 nm for the sample annealed at 350 °C.[11]

A number of previous studies have reported structural changes as a result of annealing that are relevant to this work. For example, the onset of chemical ordering in Co–Pt films via lateral and vertical diffusion, which in turn affected

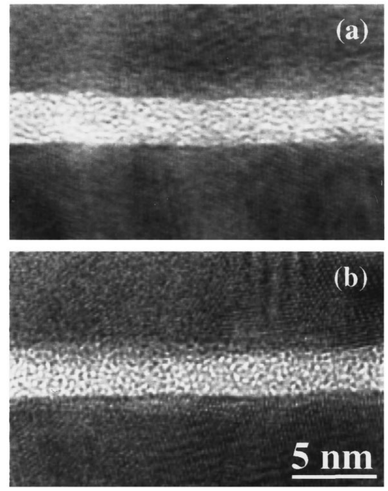

FIG. 4. High-resolution electron micrographs from the sample shown in Fig. 3. The alumina barrier region is shown (a) before annealing and (b) after annealing at 350 °C.

the magnetic and transport properties, has been reported to occur at temperatures above ~300 °C.[12] Annealing of Co/alumina multilayers has been reported[13] to cause gradual internal oxidation at the Co/alumina interfaces. In our experiments, the presence of even less than a monolayer of cobalt oxide at the FM/alumina interfaces (which would be below the detection limit for XTEM) could have a detrimental effect on the MR response. Similarly, another possibility is the diffusion of small amounts of Cr or Pt to the FM/alumina interfaces, perhaps along grain boundaries within the FM layers.

In summary, magnetic tunnel junctions formed from magnetically hard $Co_{75}Pt_{12}Cr_{13}$ and magnetically soft $Co_{88}Pt_{12}$ ferromagnetic layers with alumina tunnel barriers are thermally robust after annealing at temperatures up to ~300 °C. At higher temperatures, it is likely that the alumina and adjacent ferromagnetic layers react with one another, perhaps accounting for the observed reduction in resistance and MR for anneal treatments above ~300 °C.

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