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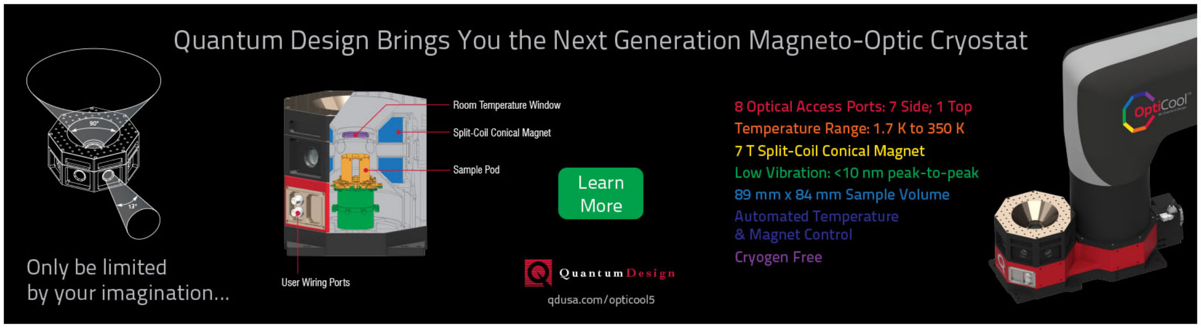
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Growth and properties of Cu_3N films and Cu_3N/γ'-Fe_4N bilayers

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Copper nitride films were grown by molecular-beam epitaxy of copper in the presence of nitrogen from a radio-frequency atomic source on (001) γ'-Fe_4N/(001)MgO or directly on MgO substrates. The structural properties of the Cu_3N films were found to be very dependent on the substrate and on the deposition temperature. At optimal growth conditions, the Cu_3N films grow epitaxial on both substrates. The Cu_3N films grown on MgO were characterized optically to be insulators with an energy gap of 1.65 eV. On γ'-Fe_4N, Cu_3N films with a thickness of only 6 nm, were grown as closed layers, epitaxial and rather smooth (root-mean-square roughness of 0.7 nm). This material has ideal properties to be used as a barrier in low resistance magnetic tunnel junctions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1459116]

Transition metal nitrides show a wide variety of properties and applications. Among them, copper nitrides have attracted considerable attention as a new material for optical storage devices, based on the rather low decomposition temperature.[1–3]

According to theoretical calculations,[4] Cu_3N is an insulator, with an energy gap of ~ 0.9 eV, whereas experimental values ranging from 0.8 to 1.9 eV were found. The structure of Cu_3N is, in itself, rather interesting. With the cubic anti-ReO_3 structure, the face-centered-cubic close-packed sites are vacant and, therefore, it is possible to insert another metallic atom (e.g., Cu and Pd). With the insertion of Cu atoms, the Cu_3N lattice undergoes a small ($\sim 1.13\%$) expansion, and the Cu_4N phase is formed.[5,6] Contrary to Cu_3N, this compound is believed to be a conductor. Similarly, Cu_3NPd compounds were synthesized, also with metallic character.[4,7]

Up until now, films of Cu_3N or Cu_3N/Cu were reported to be grown by different methods, such as rf magnetron sputtering,[1,3,8–12] dc sputtering,[13] or ion-assisted deposition.[2] The obtained films were polycrystalline on substrates like Pt/MgO, Al_2O_3, Si, or glass and amorphous on MgO and $SrTiO_3$.[8] The properties of the films were found to be very dependent on substrate and growth conditions.

In this letter, the epitaxial growth and properties of thin films of Cu_3N on γ'-Fe_4N/MgO and MgO substrates are reported. This material, with a rather low energy gap, might be used as a barrier material in low resistance magnetic tunnel junctions. Additionally, the excellent match between Cu_3N, an insulator, and γ'-Fe_4N, a ferromagnetic conductor, opens the perspective of developing an all-nitride, all-epitaxial magnetic tunnel junction.

Thin films of copper nitride were grown in a ultrahigh vacuum (UHV) chamber (base pressure of 10^{-10} mbar) by molecular-beam epitaxy (MBE) of copper in the presence of atomic nitrogen obtained from a rf atomic source. As substrates, we used (001) γ'-Fe_4N thin films grown on (001) MgO. The iron nitride films were grown in the same chamber, in a similar fashion as the copper nitride films. In previous work, we proved that this method is very effective to grow epitaxial iron nitride films.[14,15] As reported earlier, the optimal substrate temperature for the growth of γ'-Fe_4N films on (001) MgO substrates was 400 °C. At such substrate temperatures, the obtained films were of high crystal quality and rather smooth [for a ~ 33 nm film the root-mean-square (rms) roughness was 0.4 nm]. Based on the very good lattice match, the γ'-Fe_4N phase (cubic, 3.795 Å) is an ideal substrate for the epitaxial growth of Cu_3N (cubic, 3.817 Å).

Additionally, Cu_3N films were also grown directly on (001) MgO substrates, in a similar way. Here the lattice mismatch is $\sim 10\%$. In all cases, before growth, the MgO substrates were cleaned by annealing at 600 °C in 10^{-6} mbar O_2. The copper was evaporated from a Knudsen cell, at rather low deposition rates (70–130 s/Å) on γ'-Fe_4N/MgO substrates heated at 150 °C and on MgO substrates heated at 150 °C or 250 °C. The rf atomic source was operated with pure nitrogen at a gas pressure of 5×10^{-2} mbar and also with mixtures of nitrogen and hydrogen. The rf power applied was 60 W. The pressure in the UHV chamber during growth was 10^{-7} mbar.

The crystal structure was investigated by means of x-ray diffraction in a standard θ–2θ geometry (XRD) and also by performing texture measurements in a Philips X'Pert MRD system [two-dimensional-XRD (2D-XRD)]. Both measurements were done using the Cu $K\alpha$ radiation ($\lambda = 1.54$ nm). The surface morphology was probed with a NanoScope IIIa atomic force microscope (AFM). The optical properties were obtained using a Woollam variable angle spectroscopy ellipsometer. The thickness of the films was measured by Rutherford backscattering spectroscopy.

With only nitrogen in the rf atomic source, the optimal deposition temperature to obtain epitaxial layers was found to be 150 °C on γ'-Fe_4N substrates and 150 °C–250 °C on MgO. The upper limit of the deposition temperature is dictated by the N uptake in the sample: at too high temperatures no nitrogen is taken up and a pure Cu layer is grown. Also, the formation of Cu_3N films was found not to be critically dependent on the growth rate. Contrary to the growth of

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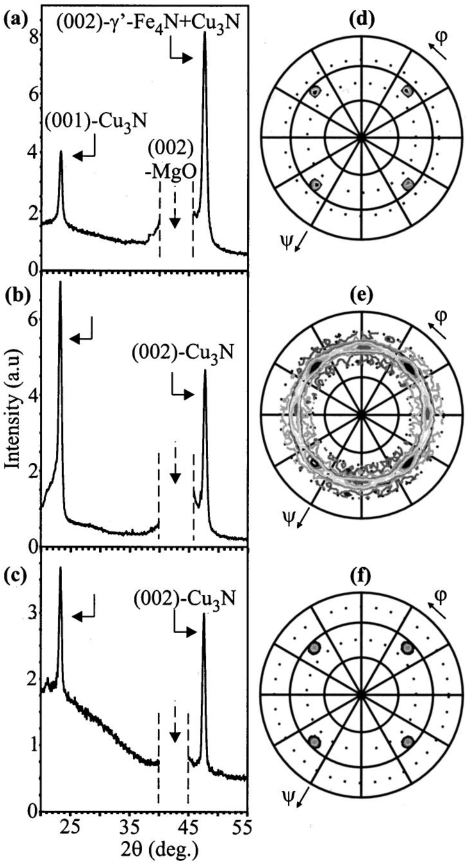

FIG. 1. X-Ray θ–2θ scans: (a) 17 nm Cu_3N/15 nmγ'-Fe_4N/MgO grown at 150 °C, (b) 18.6 nm Cu_3N/MgO grown at 150 °C, (c) 15.7 nm Cu_3N/MgO grown at 250 °C. The corresponding pole ψ–φ scans are shown in (d), (e), and (f). In all pole scans, the 2θ angle is fixed for the (111) reflection of Cu_3N.

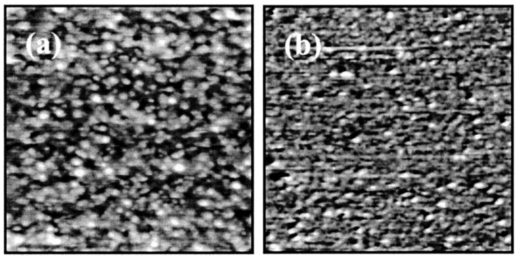

FIG. 2. AFM topographical images of Cu_3N films of different thickness (t) grown under similar conditions on γ'-Fe_4N substrates. (a) $t=17$ nm, $1\times1\ \mu m^2$ image (vertical range 25 nm; rms roughness ~2.6 nm). (b) $t=6$ nm, $1\times1\ \mu m^2$ image (vertical range 10 nm; rms roughness ~0.7 nm).

γ'-Fe_4N,[15] we found that the formation of pure Cu_3N films is less effective when hydrogen is present in a mixture with nitrogen in the rf atomic source, as compared with the case when only nitrogen is used. Possibly, part of the needed nitrogen for the formation of Cu_3N combines with hydrogen, and finally desorbs as NH_3.

Typical results of the XRD measurements for different Cu_3N samples are shown in Fig. 1, as follows: Fig. 1(a) for the bilayer structure, 17 nm Cu_3N/15 nmγ'-Fe_4N/MgO with the copper nitride film grown at 150 °C, Fig. 1(b) for a 18.6 nm Cu_3N film grown at 150 °C on MgO and (c) for a 15.7 nm Cu_3N film grown at 250 °C also on MgO. When Cu_3N is grown on a γ'-Fe_4N underlayer, the (002) reflections overlap, which results in a slightly broader peak at $2\theta=47.76°$. However, Cu_3N can be recognized by the presence of a rather intense (001) peak at $2\theta=23.3°$, as compared with the one of γ'-Fe_4N (for Cu_3N the intensity ratio of the (001) and (002) reflections is 1.16 whereas for γ'-Fe_4N this ratio is only 0.028). With bare MgO substrates, the (002) and (001) reflections of Cu_3N are clearly visible in θ–2θ scans. In all scans, only (00k) reflections corresponding to copper nitride and iron nitride are present. Therefore, we conclude that all copper nitride films have a well-defined orientation with the [100] direction normal to the (001) substrate.

To determine the in-plane orientation of the film with respect to the crystal orientation of the substrate, we performed 2D-XRD $\psi-\varphi$ pole scans with 2θ fixed at the (111) reflection of Cu_3N. Note that also the Cu_3N (111) reflection is very close to the (111) reflection of γ'-Fe_4N. The results corresponding to the three samples are presented in Figs. 1(d)–1(f). As shown in Fig. 1(d), only four sharp peaks corresponding to the (111) reflections of both Cu_3N and γ'-Fe_4N are present. Therefore, the copper nitride film grown at a deposition temperature of only 150 °C, on a matching substrate, is epitaxial and monocrystalline with the same symmetry as the iron nitride layer with respect to the MgO substrate (no in-plane rotation). For the films grown on MgO substrates, the corresponding pole scans are shown in Figs. 1(e) and 1(f). In this case, at the same deposition temperature of 150 °C as for Cu_3N films on γ'-Fe_4N (but on a different substrate), a more complex pattern with eight (111) intensity maxima is present [Fig. 1(e)]. The intensity inbetween the maxima is due to background. This pattern corresponds to an epitaxial film, with two preferred in-plane orientations, instead of only one. At higher deposition temperatures, (250 °C), the Cu_3N films are epitaxial and monocrystalline [Fig. 1(f)]. The difference in structure of the Cu_3N films on MgO obtained at different deposition temperatures could be explained on the basis of the high mismatch present between the film and the substrate (~10%) combined with a higher mobility of the Cu atoms at a higher deposition temperature. For the Cu_3N films grown on a MgO substrate we found from the 2θ values corresponding to the (002) and (111) reflections of Cu_3N, that a 18.6 nm thick film grown at 150 °C, is fully relaxed, whereas the 15.7 nm thick film grown at 250 °C, shows a slight tetragonal distortion, with a small in-plane contraction and an out-of-plane expansion.

The surface morphology of Cu_3N films of different thickness (6 nm and 17 nm) grown on γ'-Fe_4N substrates was studied in air with AFM in contact mode. For a thickness of ~17 nm, the Cu_3N films were found to be rough on a nm scale [Fig. 2(a)]. However, for the Cu_3N film of 6 nm thickness, the surface was rather smooth. [Fig. 2(b)]. Despite the rather low deposition temperature, the surface of the film has a uniform granular appearance with a rms roughness of only 0.7 nm. The difference in smoothness between the thin (6 nm) and the thicker (17 nm) Cu_3N film could be explained assuming the Stranski–Krastanov growth mode, with a critical thickness for the transition from the 2D growth regime (layer by layer) to the three-dimensional (3D) growth regime (islands) between 6 and 17 nm. Similar values (and higher) of the critical thickness for the transition from 2D to 3D growth were observed also in different systems (eg.

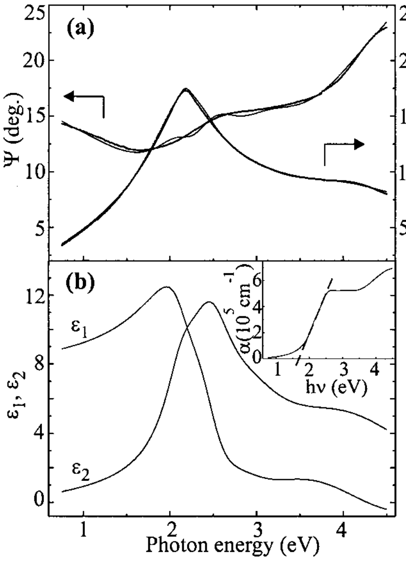

FIG. 3. (a) Measured ellipsometric parameters Ψ and Δ (thick dotted line) together with the fit of the experimental data (thin solid line) for a Cu_3N thin film (~18.6 nm) grown at 150 °C on a MgO substrate. (b) The real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function. The inset shows the absorption coefficient (α) from which the optical energy gap is estimated to be ~1.65 eV.

$YBa_2Cu_3O_{7-\delta}$). Additional x-ray photoelectron spectroscopy measurements showed, as expected, that the Cu_3N films grow as complete layers for such thin films.

Optical measurements were performed at room temperature in the 0.8–4.5 eV energy range. All spectra were taken at an angle of incidence of 70° and a fixed polarization angle of 45°. Figure 3(a) shows the measured ellipsometric parameters ψ and Δ for a Cu_3N thin film (~18.6 nm) grown at 150 °C on MgO. The experimental data were fitted taking into account the thickness of the Cu_3N film and the optical properties of the MgO substrate, with Lorentzian dielectric functions. The results of the fit are shown together with the experimental data. From the fit, the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function were calculated[16] [Fig. 3(b)]. The dependence of ϵ_1 and ϵ_2 on energy, typical for an insulator, agrees well with previously reported data. However, in our case, the magnitude of ϵ_1 and ϵ_2 is slightly higher than the values reported (all for much thicker films). This might be an effect correlated with the thickness of the films, which is much lower in our case. From the dependence of the absorption coefficient on energy as derived from our data [inset Fig. 3(b)] we estimate an energy gap of 1.65 eV. This value is in the range of data previously measured for thicker Cu_3N films grown on different substrates. For the Cu_3N film grown on MgO at 250 °C, similar results were obtained, although here a small absorption peak was present below the optical gap. Such an effect, also seen in other materials,[17] and known as the Urbach tail, might be due to absorption by impurities (in our case Cu).

Additional resistivity measurements confirmed the insulating character of all the Cu_3N films. Values in the order of ~1000 Ω cm were measured. Due to the complexity of a multilayer system for optical spectroscopy measurements and also because of lack of optical data for γ'-Fe_4N films, we could only characterize optically the Cu_3N films grown directly on MgO substrates.

In summary, this letter reports on the epitaxial growth of Cu_3N/γ'-Fe_4N bilayers and Cu_3N layers on (001) MgO substrates by MBE of copper in the presence of nitrogen from a rf atomic source. The crystal structure of the films was found to be dependent on the deposition temperature, as well as on the substrate. Films of Cu_3N grow as closed epitaxial and monocrystalline layers on epitaxial γ'-Fe_4N. Moreover, Cu_3N films with a thickness in the range of interest for tunnel junction applications were found to be rather smooth (rms roughness ~0.7 nm). On MgO substrates, the films are also epitaxial. If higher deposition temperatures (250 °C) are used, the films are also monocrystalline.

The Cu_3N films grown on MgO substrates were characterized optically to be insulators, with an optical energy gap of 1.65 eV. The present growth technique proved its potential in growing high quality insulating films, which might be good candidates for barriers in magnetic tunnel junctions.

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