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Growth and properties of \textit{Cu}_3\textit{N} films and \textit{Cu}_3\textit{N}/\textit{Y}′-\textit{Fe}_4\textit{N} bilayers

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Growth and properties of Cu₃N films and Cu₃N/γ'-Fe₄N 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'-Fe₄N/(001)MgO or directly on MgO substrates. The structural properties of the Cu₃N films were found to be very dependent on the substrate and on the deposition temperature. At optimal growth conditions, the Cu₃N films grow epitaxial on both substrates. The Cu₃N films grown on MgO were characterized optically to be insulators with an energy gap of 1.65 eV. On γ'-Fe₄N, Cu₃N 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 Cu₃N 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 Cu₃N is, in itself, rather interesting. With the cubic anti-ReO₃ 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 Cu₃N lattice undergoes a small (∼1.13%) expansion, and the Cu₃N phase is formed.5,6 Contrary to Cu₃N, this compound is believed to be a conductor. Similarly, Cu₃NPd compounds were synthesized, also with metallic character.4,7

Up until now, films of Cu₃N or Cu₃N/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, Al₂O₃, Si, or glass and amorphous on MgO and SrTiO₃.8 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 Cu₃N on γ'-Fe₄N/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 Cu₃N and γ'-Fe₄N, a ferromagnetic conductor, opens the perspective of developing an all-nitride, all-epitaxial magnetic tunnel junction.

Thin films of copper nitride were grown in an 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'-Fe₄N 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'-Fe₄N 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'-Fe₄N phase (cubic, 3.795 Å) is an ideal substrate for the epitaxial growth of Cu₃N (cubic, 3.817 Å).

Additionally, Cu₃N films were also grown directly on (001) MgO substrates, in a similar way. Here the lattice mismatch is ∼10%. In all cases, before growth, the MgO substrates were cleaned by annealing at 600 °C in 10⁻⁶ mbar O₂. The copper was evaporated from a Knudsen cell, at rather low deposition rates (70–130 s/Å) on γ'-Fe₄N/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 Kα radiation (λ = 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'-Fe₄N 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 Cu₃N films was found not to be critically dependent on the growth rate. Contrary to the growth of

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However, Cu$_3$N can be recognized by the presence of a scans, only (00\(1\)) reflections are clearly visible in \(\theta\)−2\(\theta\) scans. In all pole scans, the 2\(\theta\) angle is fixed for the (111) reflection of Cu$_3$N.

\[\gamma'\]-Fe$_4$N,\(^{15}\) we found that the formation of pure Cu$_3$N 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$_3$N combines with hydrogen, and finally desorbs as NH$_3$.

Typical results of the XRD measurements for different Cu$_3$N samples are shown in Fig. 1, as follows: Fig. 1(a) for the bilayer structure, 17 nm Cu$_3$N/15 nm \(\gamma'\)-Fe$_4$N/MgO with the copper nitride film grown at 150 °C, Fig. 1(b) for a 18.6 nm Cu$_3$N film grown at 150 °C on MgO and (c) for a 15.7 nm Cu$_3$N film grown at 250 °C also on MgO. When Cu$_3$N is grown on a \(\gamma'\)-Fe$_4$N underlayer, the (002) reflections overlap, which results in a slightly broader peak at 2\(\theta\) = 47.76°. However, Cu$_3$N can be recognized by the presence of a rather intense (001) peak at 2\(\theta\) = 23.3°, as compared with the one of \(\gamma'\)-Fe$_4$N (for Cu$_3$N the intensity ratio of the (001) and (002) reflections is 1.16 whereas for \(\gamma'\)-Fe$_4$N this ratio is only 0.028). With bare MgO substrates, the (002) and (001) reflections of Cu$_3$N are clearly visible in \(\theta\)−2\(\theta\) 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 \(\psi\)−\(\phi\) pole scans with 2\(\theta\) fixed at the (111) reflection of Cu$_3$N. Note that also the Cu$_3$N (111) reflection is very close to the (111) reflection of \(\gamma'\)-Fe$_4$N. The results corresponding to the three samples are presented in Figs. 1(d)−1(f). In Figs. 1(e) and 1(f), only four sharp peaks corresponding to the (111) reflections of both Cu$_3$N and \(\gamma'\)-Fe$_4$N 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).

The surface morphology of Cu$_3$N films of different thickness (6 nm and 17 nm) grown on \(\gamma'\)-Fe$_4$N substrates was studied in air with AFM in contact mode. For a thickness of ~17 nm, the Cu$_3$N films were found to be rough on a nm scale [Fig. 2(a)]. However, for the Cu$_3$N 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$_3$N film could be explained assuming the Stranski–Krasnov 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 in different systems (eg.
higher than the values reported of 45°. Figure 3 shows the 
measured ellipsometric parameters \( \Psi \) and \( \Delta \) (thick dotted line) 
together with the fit of the experimental data (thin solid line) 
for a Cu\(_3\)N thin film (~18.6 nm) grown at 150 °C on a MgO substrate. (b) The real (\( \varepsilon_1 \)) and imaginary (\( \varepsilon_2 \)) parts of the dielectric function. The inset shows the absorption coefficient (a) from which the optical energy gap is estimated to be ~1.65 eV.

YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\). Additional x-ray photoelectron spectroscopy 
measurements showed, as expected, that the Cu\(_3\)N 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 
\( \Psi \) and \( \Delta \) for a Cu\(_3\)N thin film (~18.6 nm) grown at 
150 °C on MgO. The experimental data were fitted taking 
into account the thickness of the Cu\(_3\)N 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 (\( \varepsilon_1 \)) and imaginary 
(\( \varepsilon_2 \)) parts of the dielectric function were calculated [Fig. 3(b)]. The dependence of \( \varepsilon_1 \) and \( \varepsilon_2 \) on energy, typical for an 
insulator, agrees well with previously reported data. However, 
in our case, the magnitude of \( \varepsilon_1 \) and \( \varepsilon_2 \) 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\(_3\)N films grown on different substrates. For the 
Cu\(_3\)N 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,\(^\text{17}\) 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\(_3\)N 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 \( \gamma'\)-Fe\(_4\)N, 
we could only characterize optically the Cu\(_3\)N films 
grown directly on MgO substrates.

In summary, this letter reports on the epitaxial growth of 
Cu\(_3\)N/\( \gamma'\)-Fe\(_4\)N bilayers and Cu\(_3\)N layers on (001) MgO 
substrates by MBE of copper in the presence of nitrogen from a 
riferrous atomic source. The crystal structure of the films 
was found to be dependent on the deposition temperature, 
and as well as on the substrate. Films of Cu\(_3\)N grow as closed 
epitaxial and monocrystalline layers on epitaxial \( \gamma'\)-Fe\(_4\)N. Moreover, 
Cu\(_3\)N 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\(_3\)N films grown on MgO substrates were charac-
terized 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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