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Navy Case No. 77,615
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PATENT APPLICATION

METHODS AND MATERIALS FOR MAGNETIC RECORDING WHILE AVOIDING THE SUPERPARAMAGéNETIC LIMIT

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to composite materials for use in magnetic recording, and methods for using such materials. More particularly, the present invention relates to materials that minimize superparamagnetism through the use of antiferromagnetic matrices for ferromagnetic particles in a recording medium.

Description of the Related Art

Magnetic recording works by reorienting the direction of the magnetizations of small, discrete regions in a magnetic recording medium, such as a video or audio tape, or a computer disk. Information is stored in the arrangement of these magnetic regions. The information density of these magnetic recording media, in principle, may be increased by decreasing the size of the magnetic domains in the recording medium. Unfortunately, there is a limit to how small these magnetic domains may be made. Magnetic domains may be made smaller by reducing the size of the ferromagnetic particles in the magnetic material. However, as these particles are made smaller, they lose the ability to keep the direction in which their magnetization is pointing constant. The problem is illustrated by FIG. 1.

As is seen in FIG. 1, the energy of a magnetic particle is a function of its orientation, i.e., the angle of rotation of the magnetization of that particle relative to some fixed direction. The difference between the maximum and minimum energies of a magnetic particle, as a function of the rotation angle, is the magnetic anisotropy ΔE_A. $\Delta E_A = E(\theta_1,\phi_1) - E(\theta_2,\phi_2)$, where θ_1,ϕ_1 and θ_2,ϕ_2 are the angles at which the energy E is at a maximum and a minimum, respectively. If ΔE_A is less than kT, where k is the boltzman constant and T is the temperature, the particles's magnetizations will rotate spontaneously (i.e., the particles behave superparamagnetically), and they will be useless for magnetic recording.

To avoid the superparamagnetic limit, efforts have been made to increase the anisotropy of magnetic materials. The anisotropy ΔE_A of a magnetic material has three principal components. They are volume anisotropy, shape anisotropy, and surface anisotropy.

The volume anisotropy is connected to the crystal symmetry of the material and is given by $\Delta E_{A\,vol}V$, where $\Delta E_{A/vol}$ is the volume anisotropy per unit volume, and V is the volume. $\Delta E_{A/vol}$ is a bulk property of a particular material phase, and is related to the tendency of certain electron orbitals to align in certain directions within a crystalline lattice. Co is used as a recording medium in part because hcp Co has a large volume anisotropy.

The shape anisotropy of particles is the portion of the anisotropy that is attributable to the shape of the particles, crystallites, or medium. Generally, a magnetic particle (such as a crystallite) will be magnetized more easily in a direction parallel to the long axis of that particle. The shape anisotropy of particles increases with increasing aspect ratio. As used herein, "particles" are inclusive of both particulate inclusions in matrices, and crystallites having some other material at the grain boundaries. However, the terms are sometimes used to distinguish one material from another.

The surface anisotropy is the anisotropy attributable to the surface, and is given by $\Delta E_{A/surf}A$, where $\Delta E_{A/surf}$ is the average magnetic surface anisotropy and A is the surface area. The surface anisotropy is believed to be related to the tendency of the magnetic moments of the atoms on the surface of the particles or crytallites to align in certain directions.

Usually, if one increases any of these contributions, the total anisotropy increases. For media with a thickness of 10 nm, it has been estimated that it is necessary to have an anisotropy larger than 305 ergs/cm^3 to stabilize the magnetization of the grains against the thermal effects and demagnetization field effects.

In particulate recording media, which uses metallic particles, the particles are coated with an oxide for chemical stability. Metallic particles are often used because they have the advantage over oxide particles in that they have larger values for their saturation magnetization. Often, the domains in magnetic film recording media are magnetically decoupled. Reducing the domain interactions reduces the noise associated with the domain structure. Thus, the distinction between film and particulate magnetic recording media is not a sharp distinction. For example, in one common material, CoCr, which is usually alloyed with other elements such as Ta, the media is inhomogeneous, having ferromagnetic Co-rich crystals surrounded by nonmagnetic Cr-rich material. The nonmagnetic material provides magnetic isolation between adjacent Co-rich crystals, and assist in the development of the proper microstructure, depending on the processing, for longitudinal or perpendicular magnetic recording.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide magnetic recording materials that are less susceptible to acting superparamagnetically.

It is a further object of this invention to provide magnetic recording materials with higher $\Delta E_{A\cdot surf}$ than have previously been available.

It is a further object of this invention to provide magnetic recording materials with higher $\Delta E_{A\cdot surf}$ than have previously been available with domain sizes than have previously been available.

It is a further object of this invention to provide magnetic recording materials with coatings that additionally retard oxidation and/or provide magnetic isolation.

It is a further object of this invention to provide methods for magnetic recording and information retrieval that take advantage of these properties.

These and additional objects of the invention are accomplished by the structures and processes hereinafter described.

The present invention is, in one aspect, a high anisotropy magnetic composite, having a plurality of ferromagnetic particles, where these ferromagnetic particles are disposed within an antiferromagnetic material, which may either be a coating for the particles, or a matrix in which the particles are disposed; and a matrix material (antiferromagnetic or otherwise). Typically, this material will be disposed on a substrate.

In another aspect, the invention is a method for magnetically recording data, comprising the step of exposing a magnetic recording medium according to the invention to a writing magnetic field.

In another aspect, the invention is a method for reading magnetically recorded data, comprising the steps of positioning a read head in proximity to a magnetic recording medium according to the invention, where the read head can read the magnetization of a region on the magnetic recording medium, and translating the read head relative to the magnetic recording medium, where the read head is thus sequentially brought into proximity to a plurality of separately written regions on the magnetic recording medium.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention will be obtained readily by reference to the following Description of the Preferred Embodiments and the accompanying drawings in which like numerals in different figures represent the same structures or elements, wherein:

FIG. 1 is a graph of the energy of a magnetized particle as a function of the angle of the magnetization of that particle.

FIG. 2 shows the section of a nominal structure for demonstrating the minimum thickness requirement for the antiferromagnetic materials used in the present invention.

FIG. 3 is a graph of coercivity of a ferromagnetic material layer versus thickness of an adjacent antiferromagnetic layer.

FIG. 4 is a sectional view of a preferred embodiment of the invention.

FIG. 5 is a sectional view of another preferred embodiment of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In conventional magnetic recording media, the ferromagnetic particles are often disposed in a nonmagnetic matrix, or have a non-ferromagnetic phase at the grain boundaries. The critical feature of the present invention is surrounding these ferromagnetic particles instead with antiferromagnetic materials. Exchange coupling between the ferromagnetic particles and the antiferromagnetic coatings or matrix will increase $\Delta E_{A/surf}$, in comparison with like particles disposed in a nonmagnetic matrix, or crystallites with a non-ferromagnetic phase at the grain boundaries, without antiferromagnetic coatings. This increase in $\Delta E_{A\ surf}$ will permit the use of smaller single domain ferromagnetic particles in the magnetic recording media without those particles becoming superparamagnetic. Skilled practitioners will recognize that the anisotropy energy of these particles must fall within the range given by:

$$kT < \Delta E_A < \mu H_{write}$$

where μ is the magnetic moment of a particle, and H_{write} is the magnetic writing field. Also, the residual magnetization must be large enough to read. The total anisotropy ΔE_A must be at least greater than kT, preferably is greater than 10 kT, and more preferably greater than 20 kT. The surface anisotropy $\Delta E_{A/surf}$ provided by the present invention preferably should be at least 0.1 kT, preferably at least 0.2 kT, more preferably kT, and still more preferably 5 kT.

The energy of a magnetic particle or crystallite will depend on the magnetization field, the applied field, and the properties of the material. An example of such a relationship is given by:

$$E = -MH_L\cos\theta - K\cos^2(\theta-\phi)$$

where M is the magnitude of $\vec{M}$, the magnetization of the particle or crystallite, H is the magnitude of $\vec{H}_L$, the average local applied field acting on the particle or crystallite, K is the anisotropy constant, θ is the direction of $\vec{M}$, and ϕ is the direction of the easy axis of magnetization. All angles are measured relative to the direction of $\vec{H}_L$. The local field includes the applied field and it is assumed that the $\vec{M}$, $\vec{H}_L$, and the easy axis of magnetization all lie in a plane. The coercive field H_c is roughly equal to the anisotropy constant K.

The antiferromagnetic materials used in the present invention must satisfy several criteria. First, these antiferromagnetic materials must have a Néel temperature T_N that is significantly greater than the operating temperature of the material (e.g., > about $2T_{op}$, > about $3/2T_{op}$, > about $4/3T_{op}$, or > about $5/4T_{op}$). Second, the antiferromagnetic material must be thick enough to provide, at the operating temperature, sufficient coupling between the antiferromagnetic material and the ferromagnetic material to increase the anisotropy of the material.

The former point is significant from a materials processing perspective. Cobalt-chromium composites are known magentic recording materials. In there materials, Co-rich crystallites are isolated from each other by Cr-rich regions. The T_N of these Cr-rich regions will be affected strongly by the purity of the chromium: T_N will be depressed by the presence of Co impurities, and the degree of depression will tend to increase with increasing Co content in the Cr-rich phase. Thus, for the materials of the present invention, it will be particularly important to prepare materials with a sufficiently high T_N to provide the necessary elevation of T_N over the operating temperature.

The latter point is also significant. Referring to FIG. 2, this structure **10** is a trilayer of antiferromagnetic NiO **14**, ferromagnetic Co **12**, and another layer of antiferromagnetic NiO **14**. It has been discovered that if an antiferromagnetic material adjacent to a ferromagnetic material is too thin, no significant increase in anisotropy will be observed at a given operating temperature. In fact, at some thickness (estimated to be below about 25 Å for NiO) there may be no increase in anisotropy.

Skilled practitioners should consider the case where the Co layers have a fixed thickness, e.g., 100 Å, and the antiferromagnetic NiO layers have a variable thickness, e.g., from 0 to 1000 Å, and the device has a selected operating temperature, e.g., 298 K. It has been discovered that the coercivity of the Co layers does not significantly increase with any thickness of NiO in the adjacent layer. Rather, the NiO layer must be at least a minimum thickness before the coercivity, and with it the anisotropy, of the Co layer increases by a significant amount. This result is depicted in FIG. 3, which plots the expected coercivity of a ferromagnetic (cobalt) layer, against the thickness of an adjacent NiO layer. As used herein, "significant" means sufficient to be useful for preactical magnetic recording applications. An increase in the coercivity of 10%, for instance, may be taken to be significant.

Thus, there will be a minimum thickness of antiferromagnetic material between adjoining regions of ferromagnetic material in preferred embodiments of the invention. This minimum thickness will depend on the specific ferromagnetic and antiferromagnetic materials selected for the invention, the operating temperature of the device, the thickness of the ferromagnetic material, and the quality, including any epitaxy, of the ferromagnetic/antiferromagnetic interface. The thickness of the antiferromagnetic layer may be expressed in terms of absolute thickness, or in terms of the percentage increase in the coercivity from the minimum coercivity to the maximum coercivity, as depicted in FIG. 3. Thus, at the baseline H_c this is 0%, and at the maximum H_c this is 100%.

Skilled practitioners should also note that as the thickness of the antiferromagnetic material increases, the volume of the structure occupied by ferromagnetic material will decrease, leading to a decrease in the saturation magnetization per unit volume. Thus, there will be an optimal amount of antiferromagnetic material in devices of the invention, and preferred ranges for antiferromagnetic materials in the invention.

Preferred thicknesses of antiferromagnetic materials (the amount of antiferromagnetic material between two regions of ferromagnetic material) will be greater than about 25 Å, greater than about 30 Å, between about 25 Å and about 1000 Å, between about 30 Å and about 750 Å, between about 35 Å and about 700 Å, between about 40 Å and about 650 Å, between about 45 Å and about 600 Å, between about 50 Å and about 550 Å, between about 60 Å and about 500 Å, between about 65 Å and about 450 Å, between about 70 Å and about 400 Å, between about 80 Å and about 350 Å, between about 85 Å and about 300 Å, between about 90 Å and about 250 Å, between about 100 Å and about 200 Å, between about 125 Å and about 175 Å, and about 150 Å.

Expressed as a percentage of increase of coercivity from $H_{c/min}$ to $H_{c/max}$, preferred ranges are from 5-100%, from 10-95%, from 15-90%, from 20-85%, from 25-80%, from 30-75%, from 35-70%, from 40-65%, from 45-60%, and from 50-55%.

As depicted in FIG. 4, a preferred embodiment of the invention **20** will have ferromagnetic particles **22** disposed in an antiferromagnetic matrix **24**. This ferromagnetic/antiferromagnetic composite **25** is disposed on a substrate **26**. The ferromagnetic particles **22** used in the present invention will be made from materials selected from the known ferromagnetic materials used for particles in magnetic recording media, including Fe, CoCr, CoCrTa, CoSm, CoCrPt, and CoNi. These particles, including their antiferromagnetic coatings, will have average diameters between about 5 nm and about 500 nm, or preferably between about 25 nm and about 250 nm.

They will have average lengths between about 20 nm and about 1000 nm. They will have average particle densities of between about 20% and about 70%. Typical aspect ratios will be between about 1 and about 50.

The antiferromagnetic materials used as matrices in the present invention will be selected from known antiferromagnetic materials, including NiO, CoO, (Co,Ni)O, Cr, Cr_2O_3, CrSb, Fe_2O_3, and MnTe.

A wide range of operating temperatures will be suitable for the present invention. Most typically, the invention will be used at about room temperature, nominally about 298 K. However, other operating temperatures are available. For example, at temperatures below room temperatures, such as at cryogenic temperatures, the magnetic materials of the invention will have higher anisotropies than at room temperature. Since kT will also be lower, the ratio of E_A to kT will be advantageously higher. Preferred cryogenic temperatures according to the present invention will be between 20 K and 200 K, between 50 K and 150 K, and (if nitrogen is used as the coolant) about 77 K. Also, operating temperatures above room temperature (e.g., 305 K, 310 K, 320 K) may be required for certain industrial applications. These too are within the scope of the invention.

Skilled practitioners will select between several known methods for making such composites, such as phase separation, evaporation, including co-evaporation, sputtering, chemical methods including using reverse micelles, and electrodeposition. To sputter such composites, for example, low pressure sputtering of the antiferromagnetic matrix material will be used to deposit a uniform antiferromagnetic layer **24**. At selected intervals, high pressure sputtering will be used to deposit particles 22 of the ferromagnetic material. Skilled practitioners will apply the known principles for controlling sputtering processes to control the size and packing density of the ferromagnetic particles 22 in the antiferromagnetic matrix 24.

Skilled practitioners will select appropriate grain sizes, orietations, and morphologies for the ferromagnetic particles, in view of the state of the art of the magnetic recording industry. Typically, ferromagnetic particles will be oriented parallel to the direction of the growth axis, or alternatively, perpendicular to the substrate. In other embodiments, ferromagnetic particles will be oriented perpendicular to the direction of the growth axis, or parallel to the substrate. Other typical embodiments of the present invention will have crystallites that are slightly tilted away from vertical by a few degrees.

In this embodiment of the invention, the substrate 26 typically will be a rigid substrate, such as for a hard disk drive. Other embodiments of the invention will be used for other media, such as floppy disks and tape.

As depicted in FIG. 5, another preferred embodiment of the invention has different particles 21 than in the preceding embodiment. These particles 21 have a ferromagnetic core 22 with an antiferromagnetic coating 32. These composite particles may then be disposed in a matrix 34 selected from a wide range of materials including all the known binders used for magnetic media, such as copolymers of vinyl chloride, isocyanates, and polyvinyl formal.

Skilled practitioners will select between several known methods for making such composite particles. Polyol processes are known for making layered metal composites. The following describe such polyol processes, and are incorporated herein, in their entireties, and for all purposes: (a) G.M. Chow et al., "Structural, morphological, and magnetic study of nano-crystalline cobalt-copper powders synthesized by the polyol process", *J. Materials Research* 10 (6) pp. 1546-54 (1995); (b) U.S. Patent No. 5,470,373, "Oxidation Resistant Copper", issued November 28, 1995 to A.S. Edelstein et al.; (c) U.S. Patent Application No. 08/565,488, Navy Case No. 76,572, "Nanostructured Metallic Powders and Films via an Alcoholic Solvent Process", filed November 30, 1995 by G.M. Chow et al.

Many metal oxides are antiferromagnetic. Oxidizing an outer layer of fine metal particles may be used to provide an antiferromagnetic coating.

Deposition techniques may also be used for making such coated particles, by passing the particles by a series of deposition sources, thereby coating the particles with a series of materials.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that

the invention may be practiced otherwise than as specifically described.

Navy Case No. 77,615
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PATENT APPLICATION

ABSTRACT OF THE DISCLOSURE

The present invention is, in one aspect, a high anisotropy magnetic composite, having a plurality of ferromagnetic particles, where these ferromagnetic particles are disposed within an antiferromagnetic material, which may either be a coating for the particles, or a matrix in which the particles are disposed; and a matrix material (antiferromagnetic or otherwise). Typically, this material will be disposed on a substrate. In another aspect, the invention is a method for magnetically recording data, comprising the step of exposing a magnetic recording medium according to the invention to a writing magnetic field. In another aspect, the invention is a method for reading magnetically recorded data, comprising the steps of positioning a read head in proximity to a magnetic recording medium according to the invention, where the read head can read the magnetization of a region on the magnetic recording medium, and translating the read head relative to the magnetic recording medium, where the read head is thus sequentially brought into proximity to a plurality of separately written regions on the magnetic recording medium.

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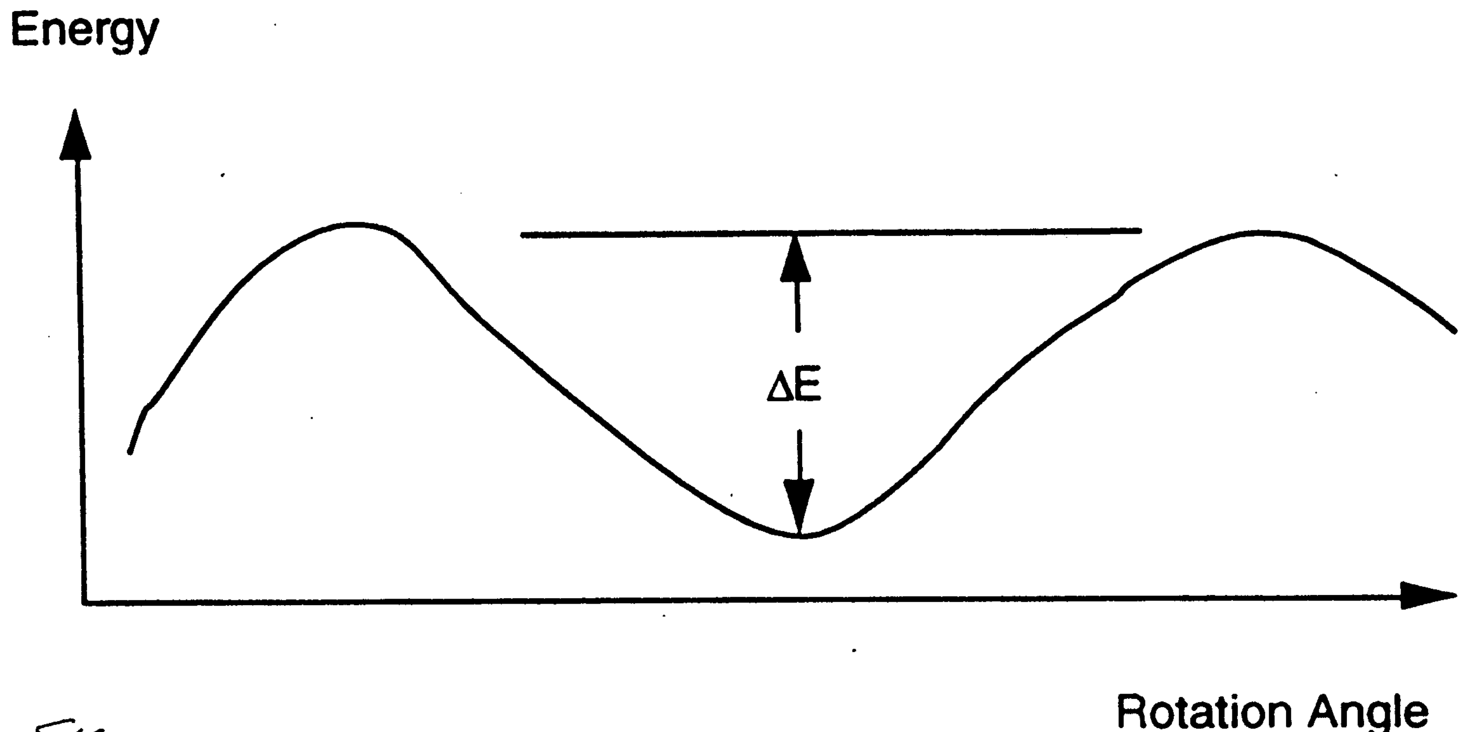

FIG. Figure 1 . Energy of Magnetic Particle as a function of its angle of rotation.

For the particles magnetic orientation to be stable, Δ E must be greater than kT. Since ΔE is usually proportional to the size of the particle, this condition becomes increasingly difficult to fulfill if the particle size is decreased. The conventional way of trying to overcome this limitation is too increase the anisotropy. Co was used in magnetic recording media because it has a large anisotropy energy.

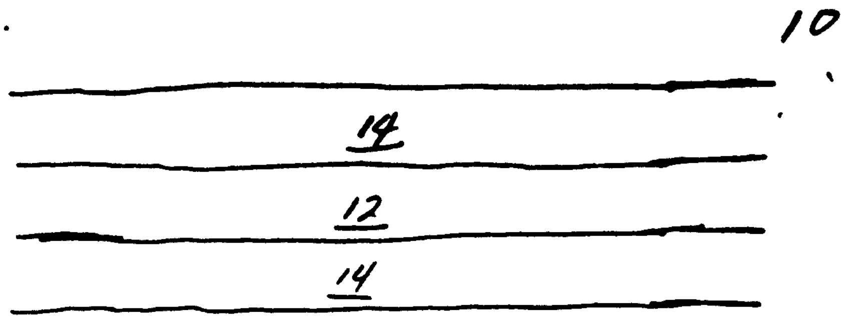

FIG. 2

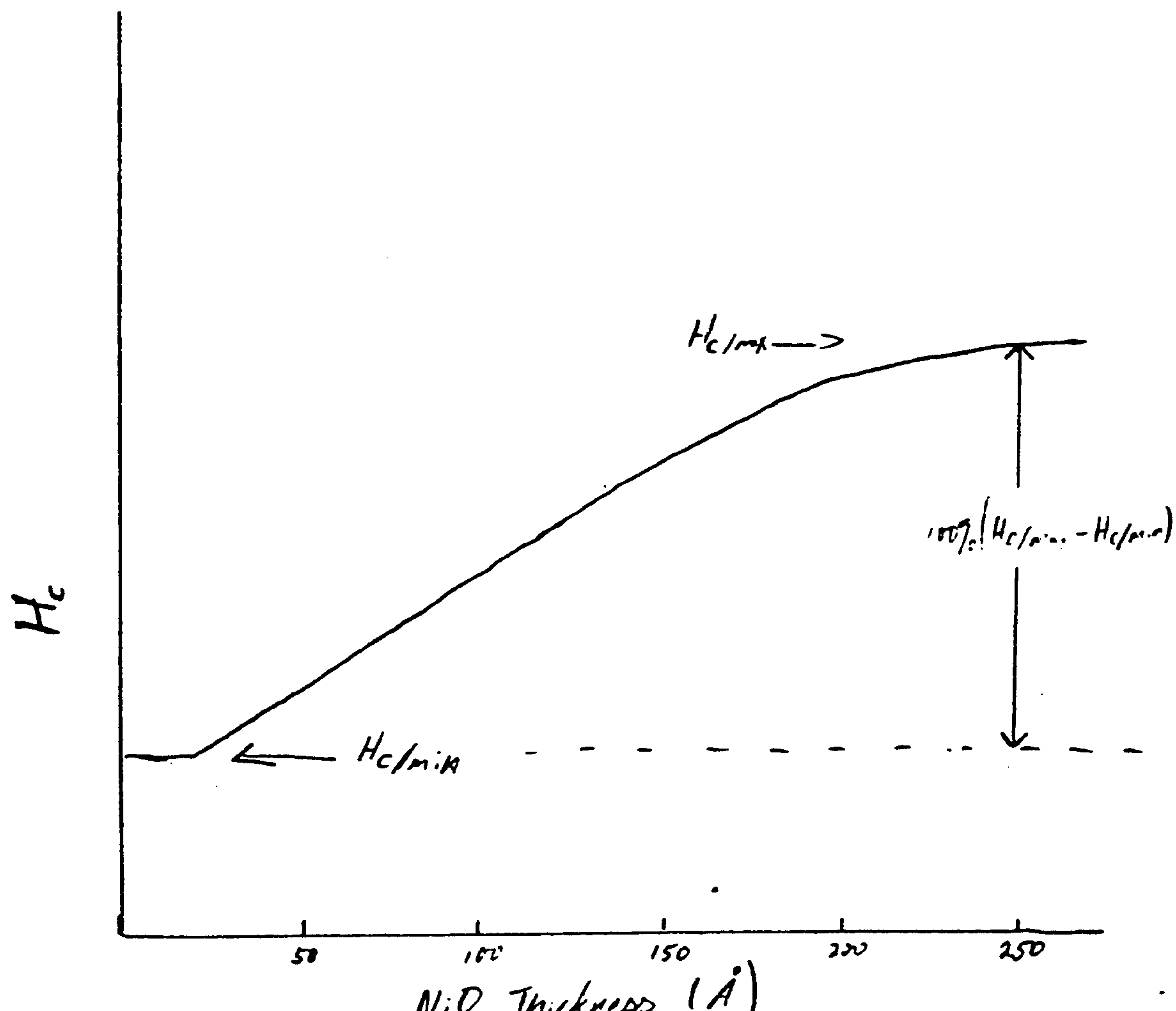

FIG. 3

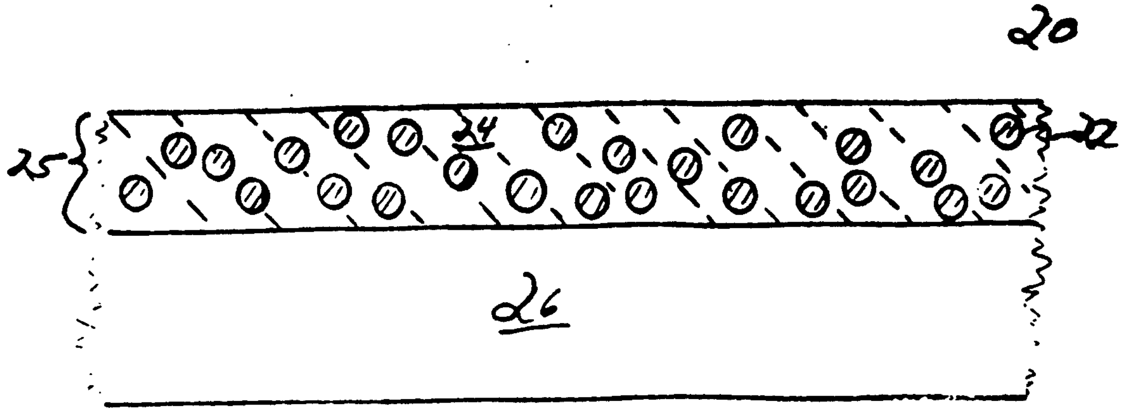

FIG. 4

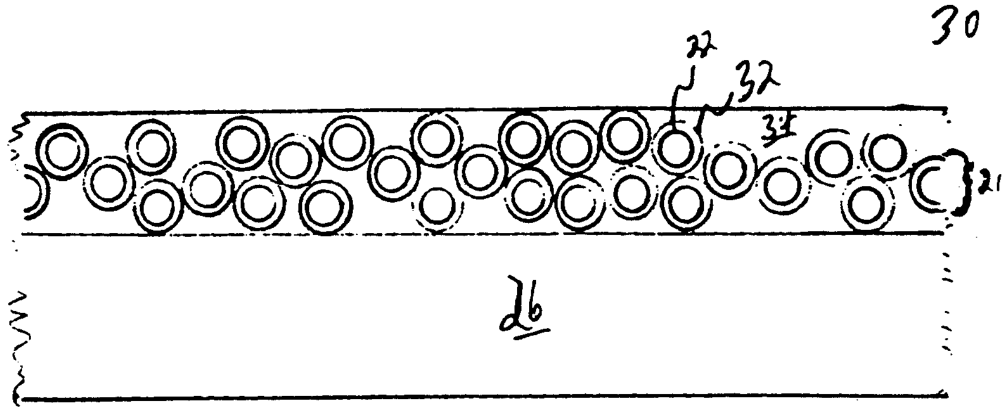

FIG. 5