US 20120236528A1

(19) **United States**
(12) **Patent Application Publication**
Le et al.

(10) **Pub. No.: US 2012/0236528 A1**
(43) **Pub. Date: Sep. 20, 2012**

(54) **MULTILAYER EMI SHIELDING THIN FILM WITH HIGH RF PERMEABILITY**

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(21) Appl. No.: **13/512,638**

(22) PCT Filed: **Nov. 19, 2010**

(86) PCT No.: **PCT/US10/57372**

§ 371 (c)(1),
(2), (4) Date: **May 30, 2012**

Related U.S. Application Data

(60) Provisional application No. 61/265,893, filed on Dec. 2, 2009.

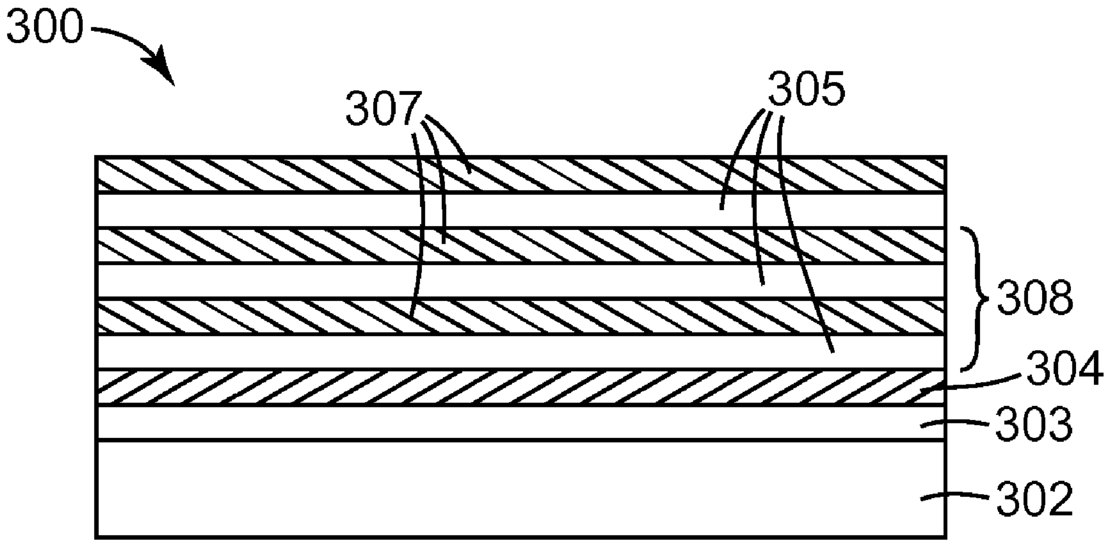
Publication Classification

(51) **Int. Cl.**
H05K 9/00 (2006.01)
C23C 16/06 (2006.01)
C23C 16/56 (2006.01)

(52) **U.S. Cl.** **361/818**; 174/391; 427/58; 427/124

(57) **ABSTRACT**

A flexible multilayer electromagnetic shield is provided that includes a flexible substrate, a thin film layer of a first ferromagnetic material with high magnetic permeability disposed upon the substrate and a multilayer stack disposed upon the first ferromagnetic material. The multilayer stack includes pairs of layers, each pair comprising a polymeric spacing layer and a thin film layer of at least a second ferromagnetic material disposed on the spacing layer. At least one or more of the spacing layers includes an acrylic polymer. Also methods of making the flexible multilayer electromagnetic shield are provided.



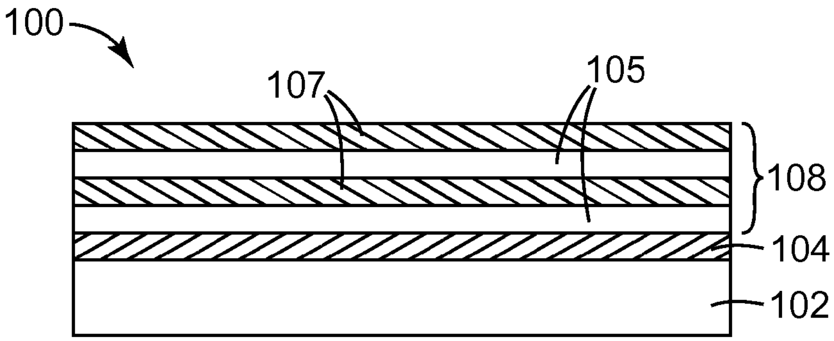


Fig. 1

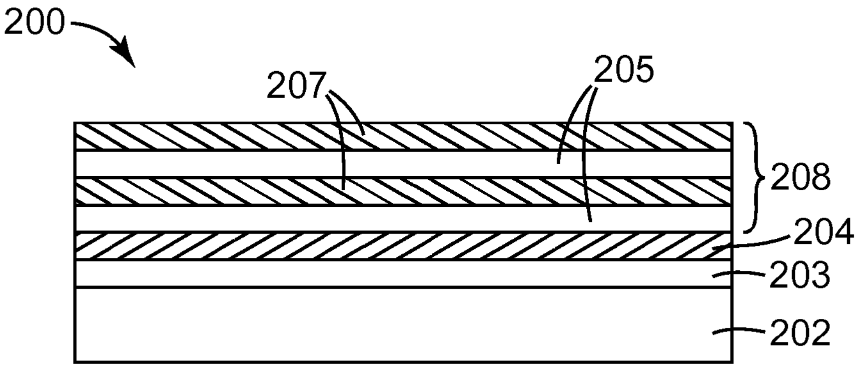


Fig. 2

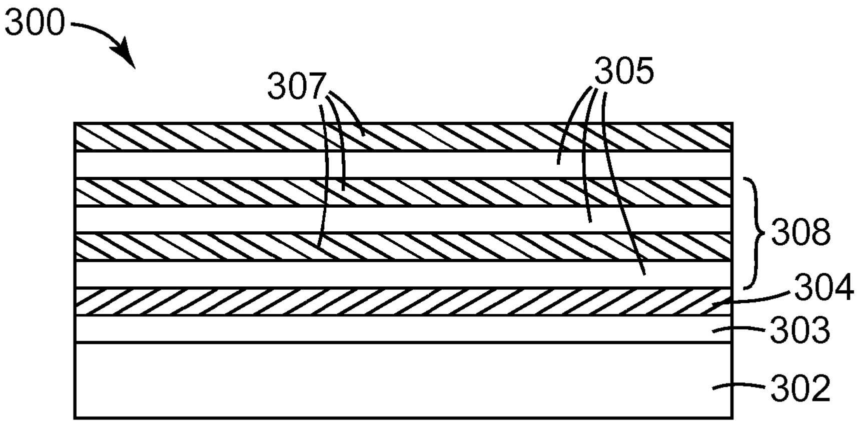


Fig. 3

MULTILAYER EMI SHIELDING THIN FILM WITH HIGH RF PERMEABILITY

FIELD

[0001] Multilayer thin films are provided that have high RF permeability and can be useful for electromagnetic interference shielding and suppression

BACKGROUND

[0002] Miniaturization of electronic devices and high frequency electronic circuits have created a demand for compact and flexible electromagnetic interference/electromagnetic compatible (EMI/EMC) material that also can suppress the degrading effect of electromagnetic interference originating in the devices and circuits or originating in the environment. Additionally EMI/EMC materials can be needed to comply with the electromagnetic compatibility (EMC) specifications for EMI control. EMI control can include EMI shielding, absorption, and/or suppression. Electrically conducting materials can be utilized to primarily provide shielding of electromagnetic radiation.

[0003] Lossy magnetic material with high permeability over a certain radiofrequency (RF) range can also be useful to attenuate or suppress the high frequency common mode EMI noise on transmission lines as most noise frequency is usually higher than that of the circuit signal. For EMI suppression, ferrites are widely used. However, they are bulky and may not be suitable for compact devices or in products that have space limitations. Furthermore, the upper limit of frequency suppression in ferrites is on the order of several hundred megahertz (MHz).

SUMMARY

[0004] Thus, there is a need for thin, flexible materials that have high magnetic permeability in the radiofrequency (RF) range. There is a need for materials that can suppress radiofrequency energy over a wider range of frequencies than is currently available in ferrites. Soft magnetic alloys can provide higher permeability at higher frequencies. For example, alloys of NiFe, CoNbZr, FeCoB, nanocrystalline Fe-based oxides and nitrides, and boron-based amorphous alloy are useful in this regard. In today's wireless and compact electronics environment, there is also a need to be able to provide EMI control at high frequencies such as, for example, in the 1-6 gigahertz (GHz) range. And in the electronics industry, as devices are becoming more compact, thinner is better.

[0005] In one aspect, a flexible multilayer electromagnetic interference shield is provided that includes a flexible substrate, a thin film layer of a first ferromagnetic material with a high magnetic permeability disposed upon the flexible substrate, and a multilayer stack disposed upon the first ferromagnetic material, the multilayer stack comprises pairs of layers, each pair comprising a spacing layer and a thin film layer of a second ferromagnetic material disposed on the spacing layer. One or more of the spacing layers comprises an acrylic polymer. The spacing layer is preferably a dielectric layer or a non-electrically conductive material to suppress the Eddy current effect. The spacing layer can be made of a ferromagnetic material with relatively lower magnetic permeability.

[0006] In another aspect, a method for making a flexible

film layer of a first ferromagnetic material upon the substrate, vapor coating and curing an acrylic polymer upon the first ferromagnetic material to form a first polymeric spacing layer, and vapor depositing a thin film of a second ferromagnetic material upon the first spacing layer.

[0007] In this application:

[0008] "adjacent" refers to layers in the provided filters that are in proximity to other layers. Adjacent layers can be contiguous or can be separated by up to three intervening layers;

[0009] "alloy" refers to a composition of two or more metals that have physical properties different than those of any of the metals by themselves;

[0010] "contiguous" refers to touching or sharing at least one common boundary;

[0011] "dielectric" refers to material that is less conductive than metallic conductors such as silver, and can refer to semiconducting materials, insulators, or metal oxide conductors such as indium-tin-oxide (ITO);

[0012] "electromagnetic interference (EMI) shielding" refers to the reflection or absorption of at least one of the components of electromagnetic waves;

[0013] The provided flexible multilayer electromagnetic shields can shield or/and suppress radiofrequency energy over a wide range of frequencies. By using thin layers of ferromagnetic material interlayered with spacing materials and by adjusting the numbers of layers, thicknesses of layers, and materials, electromagnetic interference control at high frequencies can be achieved, for example, in the 1-6 gigahertz range. Furthermore, by using vapor-condensed acrylic spacing layers the provided shields can be manufactured in a continuous, roll-to-roll manner.

[0014] The above summary is not intended to describe each disclosed embodiment of every implementation of the present invention. The brief description of the drawing and the detailed description which follows more particularly exemplify illustrative embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. **1** is a schematic of an embodiment of a provided electromagnetic shield.

[0016] FIG. **2** is a schematic of an embodiment of a provided electromagnetic shield that includes a buffer layer disposed upon the substrate.

[0017] FIG. **3** is a schematic of an embodiment of a provided electromagnetic shield that includes a buffer layer and a multilayer stack comprising 4 layers.

DETAILED DESCRIPTION

[0018] In the following description, reference is made to the accompanying set of drawings that form a part of the description hereof and in which are shown by way of illustration several specific embodiments. It is to be understood that other embodiments are contemplated and may be made without departing from the scope or spirit of the present invention. The following detailed description, therefore, is not to be taken in a limiting sense.

[0019] Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in sought to be obtained by those skilled in the art utilizing the teachings disclosed herein. The use of numerical ranges by endpoints includes all numbers within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

[0020] With the growing trend of miniaturization and portability of multifunctional high speed and high frequency personal electronic devices, such as mobile phone or personal digital assistant (PDA) devices, as well as near field communication (NFC) devices, there is a growing need for the control of electromagnetic interference (EMI) and electromagnetic crosstalk. Meeting this need can be challenging. Radiated EMI noise may need to be controlled in such electronic devices in order to limit its degradative effects, such as, for example, extraneous noise in the radiofrequency (RF) spectrum, and health hazards in the environment. In addition compliance with governmental specification may require control of EMI and electromagnetic crosstalk. Materials are known that can provide EMI shielding and can suppress EMI emissions and thus control electromagnetic interference and noise.

[0021] Magnetic materials with high RF permeability can provide EMI shielding or suppression in miniaturized multifunctional electronic devices. Thin conductive magnetic materials can be effective EMI shields for small devices due to their relatively thin skin depth and can be especially effective for near field magnetic shielding. Lossy magnetic materials can be used attenuate or suppress high frequency harmonic noise, common-mode EMI noise on transmission lines, cables, and interconnects, or can be integrated into micro-scale semiconductor circuits. The advantage of using magnetic thin films to suppress EMI noise is related to their high RF impedance, which is proportional to the permeability, frequency, volume/dimension of the magnetic material. Magnetic materials have a complex permeability, $\mu=\mu'-i\mu''$ that changes with frequency. Materials with a high RF permeability having a high μ'' can be used to obtain high loss of unwanted high frequency noise with a relatively small volume of material. Materials with a high μ' can be used for near field magnetic shielding for NFC devices which, for example, can improve the reading range for high frequency radio frequency identification tags (HF RFID tag) on metal surfaces as disclosed, for example, in U.S. Pat. No. 7,315,248 (Egbert).

[0022] Shielding against EMI is commonly accomplished by reflecting and/or absorbing the incident electromagnetic waves. A large impedance mismatch between the incident medium and the shielding material can lead to relatively high reflectance. As a wave passes through shielding material, its amplitude is attenuated exponentially as a function of skin depth. Due to cost constraints most EMI shielding materials operate simply by reflection. However, many applications can benefit by absorption of the EMI since reflected EMI can also cause additional interference. Non-magnetic metals such as silver, gold, copper, and aluminum, can have high electrical conductivities and can be useful for EMI shielding. However, the metals which are ferromagnetic can be less electrically conductive but can have much higher magnetic permeabilities than other metals. As such, they can be useful for shielding against EMI and particularly for shielding against the magnetic component of EMI. Shielding materials with high magnetic permeability and high electrical conductivity can develop low surface impedance with thinner skin depth that

rents to allow the incident EMI waves to penetrate the shielding material. Permalloy, which is an alloy of approximately 19 mole % Fe and 81 mole % Ni, and has zero magnetostriction, is a very useful, versatile, and relatively inexpensive material with high magnetic permeability. Permalloy alloy can have from about 18 mole % to about 20 mole % Fe and from about 80 mole% to about 82 mole % Ni. By zero magnetostriction it is meant that the permeability does not change with stress.

[0023] Magnetic thin films with high RF permeability can be lossy in a high-frequency range, especially in the gigahertz frequency range, where most of the bulk and the composite ferrite materials have only a small loss generation per thickness, can be advantageous for suppression applications.

[0024] Thin ferromagnetic films are known to exhibit the highest possible RF permeability of known magnetic materials. However, with the increase of film thickness, the RF permeability can degenerate because of both effects of eddy currents and out-of-plane magnetization. For these effects to be reduced, films that include multiple layers of thin ferromagnetic layers can be useful. Multilayer constructions of alternating layers of materials with high magnetic permeability and non-magnetic spacing layers have been previously disclosed, for example, in U. S. Pat. No. 5,083,112 (Piotrowski et al.) and U.S. Pat. No. 5,925,455 (Bruzzone et al.) as well as in an article authored by C. A. Grimes, "EMI shielding characteristics of permalloy multilayer thin films", *IEEE Aerospace Applications Conf Proc., IEEE, Computer Society Press Los Alamitos,* IEEE, California, USA (1994), pp. 211-221. For example, multilayer, thin film, electronic article surveillance systems which are used for protecting store merchandise and library books can have multiple layers of a magnetic thin film, such as Permalloy, interspaced with a film, such as an inorganic oxide of silicon or aluminum.

[0025] A flexible multilayer electromagnetic interference shield is provided that includes a flexible substrate. The substrate is typically a polymer film. Typical substrates can be smooth or textured, uniform or non-uniform and flexible. Polymer films can be suitable for roll-to-roll manufacturing processes. Substrates can also contain other coatings or compounds, for example, abrasion-resistant coatings (hardcoats). Substrates can include flexible plastic materials including thermoplastic films such as polyester (e.g., PET), polyimide, polyolefin, polyacrylate (e.g., poly(methyl methacrylate), PMMA), polycarbonate, polypropylene, high or low density polyethylene, polyethylene naphthalate, polysulfone, polyether sulfone, polyurethane, polyamide, polyvinyl butyral, polyvinyl chloride, polyvinylidenefluoride (PVDF), fluorinated ethylene propylene (FEP), and polyethylene sulfide; and thermoset films such as epoxy, acrylate, cellulose derivatives, polyimide, polyimide benzoxazole, polybenzoxazole, and high T_g cyclic olefin polymers. Typically, the substrate can have a thickness of from about 0.01 mm to about 1 mm. Substrates can also be metal foils, flexible printed circuits, printed circuit boards, or any other article on which the multilayer construction can be formulated on or applied to.

[0026] Flexible substrates can also be releasable polymer webs such as paper coated with a release liner. Releaseable polymer webs are well known to those of ordinary skill in the art of coatings. Flexible substrates can also include thin polymer coatings on releaseable polymer web. Thin polymer coatings can be epoxy coating, acrylic coating, and can be therseparated from the rest of the construction yielding ultra-thin products at application. An adhesive can be used to attach the multilayer construction to an electronic device after it has been removed from a releaseable polymer web.

[0027] The provided flexible multilayer electromagnetic interference shield includes a thin film layer of a first ferromagnetic material with a high magnetic permeability disposed upon the flexible substrate. These materials typically include ferromagnetic materials such as Permalloy as discussed above. Other ferromagnetic materials and alloys comprise iron, cobalt, or nickel can be used, including FeN. A multilayer stack is disposed upon the first ferromagnetic material. The multilayer stack includes pairs of layers. Each pair includes a spacing layer and a thin film of at least a second ferromagnetic material disposed upon the spacing layer. One or more of the ferromagnetic material layers may be of the same or different compositions and may have the same or different thicknesses. Each of the thin film layers of ferromagnetic materials have a thickness from about 10 nanometers (nm) to about 1 micrometer (μm), from about 20 nm to about 500 nm, or even from about 30 nm to about 200 nm.

[0028] The spacing layers can include at least one acrylic polymer. One or more of the spacing layers can include an acrylic polymer. If more than one spacing layer includes an acrylic polymer, each spacing layer may include an acrylic polymer having the same or different composition. Furthermore, the thicknesses of each of the layers can be the same or different. For example, the layers can include one or more acrylic polymer spacing layers having a thickness of from about 10 nm to about 50 μm, from about 10 nm to about 1 μm, or even from about 50 nm to about 500 nm. In the provided shields, the multilayer stack can include from 2 to about 100, from about 4 to about 50, from about 6 to about 30, from about 6 to about 20, or even from about 6 to about 12 pairs of layers. There may be more than one multilayer stack in the provided shields. If there are multiple multilayer stacks there can be additional spacing layers (one or more) in between each of the multilayer stacks.

[0029] The provided flexible multilayer electromagnetic interference shields can also include a buffer layer between the substrate and either the thin film layer of a first ferromagnetic material with a high magnetic permeability or the multilayer stack polymer coating can be utilized for adjust mechanical properties of the multilayer coating. Polymer coatings can also be used as a stress-buffered layer for the multilayer stack to improve adhesion of the stack coating and substrate, to eliminate curling, and to enable multilayer constructions having a large number of bilayers, which, without the buffer coating would be limited to a few bilayer stacks without delaminating and curling. For EMI shield application, polymer coatings can be also used as spacer layers to improve durability and flexural fatigue of the coating, especially for EMI shielding of flexible printed circuit, where flexural endurance is required.

[0030] The polymer buffer layer can also be engineered to induce various degrees of crack patterns in the multilayer coating, therefore, minimize surface conductance, which can minimize reflection loss and Eddy current effects where desirable for EMI suppression application. Patterning the multilayer coating can also help to suppress eddy currents for RFID application. Useful buffer layers include thermoset epoxy coatings. The epoxy coatings can be coated on release

induce the epoxy and multilayer stack to crack, which can help to minimize the coating stress, curling and delamination. Other materials for buffer layers can include acrylics and thermoplastic adhesives.

[0031] Each pair in the multilayer stack can include a spacing layer. If there is more than one magnetic layer in the multilayer stack then one or more of the spacing layers includes an acrylic polymer. Typically the acrylic polymer can be crosslinked. Crosslinked polymer layers are important during the fabrication of the multilayer stacks. As discussed later, one efficient way of making the multilayer stacks (and the shields, in some cases) is to alternate deposition of the magnetic materials with vapor condensation polymerization of the acrylic spacing layers. It has been unexpectedly found that crosslinked acrylic polymer systems made by vapor condensation polymerization of monomer systems are able to withstand the heat of subsequent vapor deposition of metallic coatings. The processes used to make the provided multilayer shields is discussed later in this specification and is exemplified in the example section.

[0032] Useful crosslinked polymeric layers can be formed from a variety of organic materials. Typically, the polymeric layer is crosslinked in situ atop substrate or the previously deposited layer. If desired, the polymeric layer can be applied using conventional coating methods such as roll coating (e.g., gravure roll coating) or spray coating (e.g., electrostatic spray coating), then crosslinked using, for example, UV radiation. Typically, the polymeric layer can be formed by flash evaporation, vapor deposition, and crosslinking of a monomer. Volatilizable acrylamides (such as those disclosed in U. S. Pat. Publ. No. 2008/0160185 (Endle et al.)) and (meth)acrylate monomers are typically used in such a process, with volatilizable acrylate monomers being especially preferred. Fluorinated (meth)acrylates, silicon (meth)acrylates and other volatilizable, free radical-curing monomers can be used. Coating efficiency can be improved by cooling the support. Particularly preferred monomers include multifunctional (meth)acrylates, used alone or in combination with other multifunctional or monofunctional (meth)acrylates, such as phenylthioethyl acrylate, hexanediol diacrylate, ethoxyethyl acrylate, phenoxyethyl acrylate, cyanoethyl (mono)acrylate, isobornyl acrylate, isobornyl methacrylate, octadecyl acrylate, isodecyl acrylate, lauryl acrylate, β-carboxyethyl acrylate, tetrahydrofurfuryl acrylate, dinitrile acrylate, pentafluorophenyl acrylate, nitrophenyl acrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, 2,2, 2-trifluoromethyl(meth)acrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, neopentyl glycol diacrylate, propoxylated neopentyl glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol diacrylate, bisphenol A epoxy diacrylate, 1,6-hexanediol dimethacrylate, trimethylol propane triacrylate, ethoxylated trimethylol propane triacrylate, propylated trimethylol propane triacrylate, 2-biphenyl acrylate, tris(2-hydroxyethyl)-isocyanurate triacrylate, pentaerythritol triacrylate, phenylthioethyl acrylate, naphthloxyethyl acrylate, EBECRYL 130 cyclic diacrylate (available from Cytec Surface Specialties, West Paterson, N.J.), epoxy acrylate RDX80095 (available from Rad-Cure Corporation, Fairfield,

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