A method of forming an array of pointed structures comprises depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate an array of surface protrusions, and solidifying the surface protrusions to form the array of pointed structures. The pointed structures may have a tip radius ranging from approximately 10 µm to approximately 25 µm. Solidifying the surface protrusions may be carried out at a temperature ranging from approximately 10 degrees C. to approximately 30 degrees C.

**References Cited**

U.S. PATENT DOCUMENTS

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Date</th>
<th>Inventor/Assignee</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,946,613 A</td>
<td>8/1990</td>
<td>Ishikawa</td>
</tr>
<tr>
<td>5,628,659 A</td>
<td>5/1997</td>
<td>Xie et al.</td>
</tr>
<tr>
<td>5,861,707 A</td>
<td>1/1999</td>
<td>Kumar</td>
</tr>
<tr>
<td>5,916,641 A</td>
<td>6/1999</td>
<td>McArdle et al.</td>
</tr>
<tr>
<td>5,935,454 A</td>
<td>8/1999</td>
<td>Tada et al.</td>
</tr>
<tr>
<td>5,954,991 A</td>
<td>9/1999</td>
<td>Hong et al.</td>
</tr>
<tr>
<td>6,056,889 A</td>
<td>5/2000</td>
<td>Tsuda et al.</td>
</tr>
<tr>
<td>6,057,172 A</td>
<td>5/2000</td>
<td>Tomihari</td>
</tr>
<tr>
<td>6,149,857 A</td>
<td>11/2000</td>
<td>McArdle et al.</td>
</tr>
<tr>
<td>6,174,449 B1</td>
<td>1/2001</td>
<td>Alwan et al.</td>
</tr>
<tr>
<td>6,290,894 B1</td>
<td>9/2001</td>
<td>Raj et al.</td>
</tr>
<tr>
<td>6,391,391 B1</td>
<td>5/2002</td>
<td>Martin et al.</td>
</tr>
<tr>
<td>6,786,174 B2</td>
<td>9/2004</td>
<td>Schleier-Smith</td>
</tr>
<tr>
<td>6,844,378 B1</td>
<td>1/2005</td>
<td>Martin et al.</td>
</tr>
<tr>
<td>6,960,528 B2</td>
<td>11/2005</td>
<td>Chen et al.</td>
</tr>
</tbody>
</table>

* cited by examiner

Primary Examiner — Christina Johnson
Assistant Examiner — Xue Liu
Attorney, Agent, or Firm — Christopher O. Edwards

**ABSTRACT**

A method of forming an array of pointed structures comprises depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate an array of surface protrusions, and solidifying the surface protrusions to form the array of pointed structures. The pointed structures may have a tip radius ranging from approximately 10 nm to approximately 25 µm. Solidifying the surface protrusions may be carried out at a temperature ranging from approximately 10 degrees C. to approximately 30 degrees C.

30 Claims, 8 Drawing Sheets
METHOD OF FORMING POINTED STRUCTURES

CROSS REFERENCE TO RELATED APPLICATIONS


ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

FIELD OF THE INVENTION

The present invention relates to a method of forming pointed structures and, more particularly, to a method of forming nanoscale pointed structures using a ferrofluid.

BACKGROUND OF THE INVENTION

Nanoscale pointed structures are known in the art. Such structures may be formed as individual pointed structures or they may be formed in arrays, such as, for example, nanotip arrays. There are a broad variety of applications for pointed structures, including use as stylus for surface profiling, scanning probe microscopy probe tips, and field emitter arrays. As field emitter arrays, these structures can be used to provide an electron source in applications such as, for example, microwave power amplifiers, flat panel displays, electron microscopy, electron beam lithography, photocathode detectors, and space propulsion systems.

Conventional techniques of forming nanoscale pointed structures include lithography, various types of etching, chemical vapor deposition, and manipulation of optical fibers and carbon nanotubes. There are a number of limitations associated with these conventional techniques. Some of the techniques are limited to the production of small arrays of structures. Others produce arrays of structures having wide distributions of height and/or aspect ratio. Still other techniques produce high quality arrays, but require equipment that is prohibitively expensive and materials that require special handling and are prone to breakage.

SUMMARY OF EXEMPLARY ASPECTS

In the following description, certain aspects and embodiments of the present invention will become evident. It should be understood that the invention, in its broadest sense, could be practiced without having one or more features of these aspects and embodiments. It should also be understood that these aspects and embodiments are merely exemplary.

To overcome the drawbacks of the prior art and in accordance with the purpose of the invention, as embodied and broadly described herein, one aspect of the invention relates to a method of forming an array of pointed structures comprising depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate an array of surface protrusions, and solidifying the surface protrusions to form the array of pointed structures.

1. As used herein, “ferrofluid” means a stable colloidal suspension of nanoscale magnetic particles dispersed with one or more surfactants in a liquid carrier.

2. In another aspect, the invention relates to a method of forming at least one pointed structure, comprising depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate at least one surface protrusion, and solidifying the at least one surface protrusion to form the at least one pointed structure.

3. In a further aspect, the invention provides a pointed structure consisting essentially of magnetic particles, produced by a process comprising depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate a surface protrusion, and solidifying the surface protrusion to form the pointed structure.

4. Aside from the structural and procedural arrangements set forth above, the invention could include a number of other arrangements, such as those explained hereinafter. It is to be understood that both the foregoing description and the following description are exemplary only.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several exemplary embodiments of the invention and, together with the description, serve to explain the principles of the invention. FIG. 1 is a schematic view of a device for carrying out an embodiment of the present invention; FIG. 2 is a scanning electron micrograph of an array of pointed structures formed according to an embodiment of the present invention; FIG. 3 is a scanning electron micrograph of an array of pointed structures formed according to another embodiment of the present invention; FIG. 4 is a scanning electron micrograph of the tip of a pointed structure formed according to another embodiment of the present invention; FIG. 5 is a scanning electron micrograph of the tip of a pointed structure formed according to another embodiment of the present invention; FIG. 6 is a scanning electron micrograph of the tip of a pointed structure formed according to another embodiment of the present invention; FIG. 7 is a photograph of an array of surface protrusions on a ferrofluid formed according to another embodiment of the present invention; and FIG. 8 is a schematic view of a device for carrying out another embodiment of the present invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

Reference will now be made in detail to exemplary embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

FIG. 1 shows a device 10 for carrying out an embodiment of the method according to the invention. In one embodiment, the method of forming an array of pointed structures comprises depositing a ferrofluid 12 on a substrate 14. The ferrofluid may comprise a stable colloidal suspension of nanoscale magnetic particles dispersed with one or more surfactants in a liquid carrier. A typical ferrofluid may contain by volume about 5% magnetic particles, about 10% surfactants in a liquid carrier.
The methods described herein involve ferrofluids, which may comprise at least one magnetic material and a carrier liquid. The magnetic material may be magnetic particles or magnetic nanoparticles. Ferrofluids are materials that contain magnetic particles suspended in a liquid carrier. When a magnetic field is applied, the magnetic particles align with the field, creating a magnetic moment. This alignment can be observed as a magnetic field, which can be used for various applications such as magnetic imaging, magnetic separation, or magnetic storage.

In the context of the methods described, ferrofluids are used to create pointed structures. These structures are formed by applying a magnetic field to a ferrofluid on a substrate. The magnetic field aligns the magnetic particles in the ferrofluid, causing them to form tips or pointed structures. These structures can be further processed, for example, by evaporating the carrier liquid to solidify the surface protrusions and form the pointed structures on the substrate.

The pointed structures are controlled by the magnetic field and the composition of the ferrofluid. The size, shape, and orientation of the pointed structures can be adjusted by controlling the magnetic field strength and duration. In addition, the surfactants used in the ferrofluid can influence the formation of the pointed structures, as they can control the spacing and distribution of the magnetic particles.

The pointed structures formed according to embodiments of the invention were analyzed using X-ray diffraction and other techniques. The analysis indicated the presence of the magnetic particles with no detectable levels of the carrier fluid or the surfactant. This suggests that the carrier liquid and surfactants are efficiently removed during the formation process.

In some embodiments, pointed structures having aspect ratios of at least 10 to 20 were formed. The pointed structures were analyzed using scanning electron microscopy and photoluminescence microscopy. The pointed structures were shown to have a smooth surface and a well-defined tip. Additionally, the pointed structures showed magnetic properties, indicating the successful alignment of the magnetic particles in the ferrofluid.

In conclusion, the methods described herein provide a controlled and reproducible way to form pointed structures using ferrofluids. These structures can be used in various applications, such as magnetic imaging, magnetic separation, or magnetic storage. The ability to control the size, shape, and orientation of the pointed structures allows for tailored applications in different fields.
In one embodiment, the tips are spaced at a distance ranging from approximately 50 μm to approximately 400 μm.

According to other embodiments of the invention, the tips have a substantially identical radius. In one embodiment, the radius ranges from approximately 10 nm to approximately 25 μm. In another embodiment, the radius ranges from approximately 10 nm to approximately 750 μm.

According to another embodiment, a method of forming at least one pointed structure comprises depositing a ferrofluid on a substrate, applying a magnetic field to the ferrofluid to generate at least one surface protrusion, and solidifying the at least one surface protrusion to form the at least one pointed structure.

In one embodiment, applying a magnetic field comprises disposing a first magnetic field generating element proximate to a first surface of the substrate. As discussed above, in some embodiments, the magnetic field is produced by at least one of (i) at least one permanent magnet, (ii) at least one electromagnet, and (iii) at least one oscillating electrical field. As in the embodiments described above, other methods and devices may also be used to generate a magnetic field.

In another embodiment, applying a magnetic field further comprises disposing a second magnetic field generating element proximate to a second surface of the substrate. In yet another embodiment, the first magnetic field generating element and the second magnetic field generating element comprise permanent magnets. In this embodiment, the arrangement of two permanent magnets provides a uniform magnetic field, which tends to align the surface protrusions and maximize their aspect ratio.

In one example, an embodiment of the present invention was carried out using a ferrofluid manufactured by FERRO-TEC® under the product name EFH®. EFH® comprises 3-15% by volume magnetic (Fe₃O₄) particles suspended in a light mineral oil carrier fluid with a proprietary surfactant and has a saturation magnetization of 400 Gauss.

Approximately 1 mL of the ferrofluid 12 was spin-coated onto a first glass substrate 14, which was disposed on two glass supports 16, as shown in FIG. 8. Two more glass supports 20 and a second glass substrate 22 were disposed on an upper surface of the first glass substrate 14, as shown. A magnetic field was applied to the ferrofluid 12 using two NdFeB permanent magnets 24, each having a diameter of approximately 15 cm, a maximum magnetic field of approximately 2.5 kG, and a field gradient across the surface of the magnet of approximately 215 G/mm. One magnet 24 was disposed below the first substrate 14 and the other magnet 24 was disposed over the ferrofluid 12 on an upper surface of the second substrate 22.

The resulting magnetic field generated an array of substantially conical surface protrusions in the ferrofluid. The surface protrusions were solidified at room temperature using a fan to evaporate the surfactant, leaving an array of pointed structures consisting essentially of magnetite.

In another example, approximately 1 mL of the EFH® ferrofluid was spin-coated onto a first glass substrate. A 1 kG permanent magnet was disposed beneath the substrate. The magnetic field gradient across the magnet surface was approximately 0.061 kG/mm. A second permanent magnet was disposed over the ferrofluid on an upper surface of the second substrate. Again, the resulting magnetic field generated an array of substantially conical surface protrusions in the ferrofluid. The surface protrusions were solidified at room temperature using a fan to evaporate the surfactant, leaving an array of pointed structures consisting essentially of magnetite.
8. The method of claim 1, wherein the pointed structure field emitters have an aspect ratio of at least 1 to 3.

9. The method of claim 8, wherein the pointed structure field emitters have an aspect ratio of at least 1 to 10.

10. The method of claim 9, wherein the pointed structure field emitters have an aspect ratio of at least 1 to 20.

11. The method of claim 10, wherein the pointed structure field emitters have an aspect ratio of at least 1 to 50.

12. The method of claim 1, wherein each of the pointed structure field emitters comprises a tip.

13. The method of claim 12, wherein the tips have a substantially conical shape.

14. The method of claim 13, wherein the substantially conical shape is a compound conical shape.

15. The method of claim 12, wherein the tips are substantially evenly spaced.

16. The method of claim 15, wherein the tips are spaced at a distance ranging from approximately 50 µm to approximately 400 µm.

17. The method of claim 12, wherein the tips have a substantially identical radius.

18. The method of claim 17, wherein the radius ranges from approximately 10 nm to approximately 25 µm.

19. The method of claim 18, wherein the radius ranges from approximately 10 nm to approximately 750 nm.

20. The method of claim 1, wherein evaporating the carrier liquid is carried out at a temperature ranging from approximately 10 degrees C. to approximately 30 degrees C.

21. The method of claim 20, wherein evaporating the carrier liquid is carried out at a temperature ranging from approximately 15 degrees C. to approximately 25 degrees C.

22. The method of claim 1, further comprising coating the pointed structures with a thin film.

23. The method of claim 22, wherein the thin film comprises at least one of a semiconducting thin film, an insulating thin film, and a conducting thin film.

24. A method of forming at least one pointed structure field emitter, comprising: depositing a ferrofluid contained in a carrier liquid in one of a droplet or spin-coated form on a substrate; applying a combined uniform magnetic field substantially perpendicular to the substrate to the ferrofluid by disposing a first magnetic field generating element proximate to a first surface of the substrate and disposing a second magnetic field element generating element proximate to a second surface of the substrate to generate at least one surface protrusion; coating the pointed structure field emitters with wide bandgap semiconductors for absorbing and emitting electrons in the ultra violet wavelength region; solidifying by evaporating the carrier liquid at approximately room temperature, and aligning the at least one surface protrusion thus maximizing the aspect ratio of said protrusion to form the at least one pointed structure field emitter.

25. The method of claim 24, wherein the magnetic field is produced by at least one of (i) at least one permanent magnet, (ii) at least one electromagnet, and (iii) at least one oscillating electrical field.

26. The method of claim 25, wherein the first magnetic field generating element and the second magnetic field generating element comprise permanent magnets.

27. The method of claim 24, wherein the at least one pointed structure comprises a substantially conical tip.

28. The method of claim 27, wherein the tip has a radius ranging from approximately 10 nm to approximately 25 µm.

29. The method of claim 28, wherein the tip has a radius ranging from approximately 10 nm to approximately 750 nm.

30. The method of claim 24, wherein solidifying the at least one surface protrusion comprises evaporating a carrier liquid of the ferrofluid at a temperature ranging from approximately 10 degrees C. to approximately 30 degrees C.