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論文内容要旨

In proportion to increases in the volume of information, and storage systems have been demanded for the rise of data storage density. However, it is predicted that the storage densities of magnetic and optical recording are limited by superparamagnetic limit and diffraction limit, respectively. Solid state memory is also limited by diffraction limit because miniaturization of the solid state memory depends on the microfabrication technology using photolithography.

In order to achieve high-density data storage beyond these physical limitations, scanning probe data storage systems have been proposed as one of future ultra-high density data storage systems beyond 1 Tbits/inch^2. The scanning probe data storage system is based on scanning probe microscopy (SPM) technology. Until now, several types of SPM technologies have been developed, such as scanning tunneling microscopy (STM), atomic force microscopy (AFM), and scanning near-field optical microscopy, etc. The SPM has been a useful tool for the observation and modification of surfaces with nano- or atomic-scale resolution. This capability can be applied to data storage devices with a recording density much higher than that of conventional data storage technologies. Many researchers have proposed various recoding principles based on charge storage, changes of crystalline phase, near-field optical recording, ferroelectric polarization, thermomechanical deformation, and electrical conductance change of organic materials, etc.

In these SPM recording systems, using only a single probe, the processing speeds and data transfer rates are limited by the mechanical resonance frequency of the AFM cantilevers or feedback speed for the gap control between the probe and recording media. Consequently, multiprobes consisting of a two-dimensional array of cantilevers have been developed by microelectromechanical system (MEMS) technology in order to achieve a high data processing rate. Dynamic AFM requires complex signal processing including actuation of a cantilever, lock-in detection of vibration and gap control on individual cantilevers. From the simplicity in the distance control, the technology of contact mode AFM is advantageous for the multiprobe data storage system.

However, there are some critical issues in the multiprobe data storage system. One of these issues is wear of the tip owing to contact operation with a recording medium. In addition, if the recording principle is complex, such as using high-frequency alternating current, the total volume of the recording system becomes large due to

he complex circuits for the probe array operation.

In this study, it is proposed that a conductive polymer is used as a recording medium for the scanning multiprobe data storage system. The recording principle is based on the electrical conductance change of the conductive polymer due to an electrochemical reaction. This electrochemical reaction is caused by applying a voltage between a conductive SPM probe and the conductive polymer in contact operation even in ambient atmosphere. The data reading principle relies on the conductivity detection of the conductive polymer with application of a low voltage. The high and low conductive states of the polymer correspond to binary data. The advantage of the conductive polymer recording is that the soft polymer can reduce the wear of the tips due to the mechanical deformation of the polymer. In addition, the simple recording method relying on the conductivity change of the conductive polymer can miniaturize the total volume of the system due to the simple signal processing.

The objective of this study is that the capability and potential ability of conductive polymer as a recording medium for scanning multiprobe data storage are investigated through the formation of conductive polymer recording media and electrical modification experiment using SPM. In this study, polyaniline (PANI) was used as a conductive polymer, of which conductance depends on the redox level. The conductivity of PANI was changed by controlling the redox revel by applying voltages with SPM.

In chapter 1, the background and motivation of this study are described, and the objective of this study is leaded.

In chapter 2, the properties and the basal-conduction theories of general conductive polymers are described. In addition, the unique-conduction property depending on redox revel and the synthesis method of PANI are also shown.

In chapter 3, the electrical modification of a conductive polymer film was demonstrated using the SPM in atmosphere. The conductive polymer film was formed by spin-coating a blend of PANI and polymethylmethacrylate on Au surface to make a test specimen. The tip of the conductive SPM probe was placed in contact with the conductive polymer film and electrical modification was carried out by applying a voltage between the SPM probe and the film. The conductance image and a simultaneous topographic image were taken with SPM. In the electrical modification, it was achieved that the conductivity of the polymer film was decreased more than 20 times. Measurement of the topographic image shows no obvious change in the surface topography at the modified area. In the electrical modification with dot-array pattern, a recording bit of 150–200 nm could be formed.

In chapter 4, the reversible electrical modification of a PANI film was achieved in atmosphere. The conductive polymer film of chapter 3 was composed of two kinds of polymers. Therefore, the uniformity and surface roughness of the film were poor due to phase separation. Then, using a surface-initiated polymerization (SIP) method, a thin PANI film was formed from a self-assembled monolayer (SAM) of 4-aminothiophenol on an Au surface. Then, the electrical modification of the PANI film was demonstrated by the SPM in atmosphere. At first, the PANI film was electrically modified on rectangle area by applying a positive voltage of 3 V. Then, the conductivity of the PANI film on the rectangle decreased. Next, the PANI was modified by applying a negative voltage of − 3 V on a smaller inner rectangle. This application of negative voltage increased the conductivity of the film. Finally, the PANI was again modified in the same way by applying a voltage of 3 V. As the result, the conductivity on the modified area decreased again. From these results, it is found that the conductivity of the film can be reversibly changed by applying a voltage between the SPM and the film, depending on the polarity of the applied voltage. From X-ray photoelectron spectroscopy (XPS) measurement, it was shown that this reversible electrical modification originated in the oxidation–reduction reaction of PANI via the water in atmosphere. These experimental results indicated that the conductive polymer has a potential ability for rewritable recording media of the scanning multiprobe data storage system. In the electrical modification with dot pattern, the dot size ranged from 100 to 200 nm and the pitch ranged from 500 to 800 nm. This pitch corresponded to the recording density of 1~2 Gbits/inch^2.

In chapter 5, template-stripped gold (TSG) surface was formed in order to obtain ultra-flat Au surface. The PANI film of chapter 4 had many grains and ununiformity of conductivity. Thus, for investigating causes of the formation of grains, a PANI film was formed on the ultra-flat Au surface without Au grains. First, a gold film was sputtered on a cleaved mica. As a result, the interfacial gold became very flat due to use of the ultra-flat cleaved mica as template. Then, the gold film was transferred onto a separate substrate using gold-gold direct bonding, and the mica was mechanically stripped. As the result, the TSG surface was obtained. It was confirmed from STM and AFM measurements that atomically flat TSG surface was formed on large area by the template-stripped method. Then, the PANI film was deposited on the TSG surface using a SIP method and characterized with AFM. In the result, many grains of the PANI film were observed. The ununiformity of conductivity was also observed. Therefore, it was considered that these grains were caused by the aggregation of PANI molecular chains, and the aggregation is one of the causes which raised the ununiformity in conductance state of the PANI film.

In chapter 6, PANI dot array as a patterned medium was fabricated using electron beam (EB) lithography. The experiment of chapter 5 shows that it was difficult to obtain a uniform PANI film in nanometer scale due to the aggregation of the PANI molecular chains. Therefore, conductive polymer patterned medium was proposed, which made of conductive polymer islands surrounded by an insulator matrix. It is expected that the patterned medium prevents the random aggregation of the PANI chains. The aggregation is limited by inner hollows. Therefore, the uniform PANI dot array without the random aggregation can provide the reduction of defects, resulting in an improvement of recording reliability compared with the uniform PANI film. Dots pattern was defined to EB resist using EB lithography and the PANI dot array was fabricated by using electrolytic polymerization from the bottom of the Au film. In the result, the PANI dots array with the dot pitch of 350 nm was formed. This pitch corresponded to the recording density of 5 Gbits/inch^2. In electrical modification experiment, the conductivity of the PANI dots could be reversibly changed by the application of appropriate voltage using the conductive SPM tip. The electrical modification of individual dots could be also carried out. The ratio of the high conductivity to the low conductivity was more than 100. It was demonstrated that the conductive polymer has the potential ability for the patterned media of scanning probe data storage systems. In the investigation of repeatability of conductivity change, the conductivity of the patterned medium was reversibly changed over 20 erase–write cycles with voltages of ±1 V. However, the conductance decreased with increasing the erase–write cycles. At a lower modification voltage, degradation of the PANI due to erase–write cycles occurs more gradually than at higher modification voltage. This conductance decrease may be attributed to desorption of dopant, crosslink or break of the PANI chains due to application of high voltage and Joule heating.

In chapter 7, conductive polymer dots pattern as a patterned medium was formed using diblock copolymer lithography (DCL). In chapter 6, the patterned medium with a dot pitch of 350 nm was fabricated by EB lithography. However, it was difficult to fabricate smaller dot-pitch pattern. The conductive polymer patterned medium was fabricated by using the microphase separation of diblock copolymer in order to easily form high-density dots pattern higher than that by EB lithography. The fabrication of PANI dots pattern using DCL was carried out with the following process. First, a photoresist layer was formed on the Au surface as the insulator matrix of the patterned media. Next, after Al was sputtered, a polystyrene-*block*-polymethylmethacrylate (PS-*b*-PMMA) was spin-coated. Then, the microphase-separated structure of PS-*b*-PMMA was generated by annealing. As a result, the semispherical structure of PMMA surrounded by PS matrix was formed on the surface. The average diameter and the domain pitch of PMMA were 40 and 80 nm, respectively. Then, by removal of the PMMA domain, semispheric dots hollow pattern was formed. Next, the photoresist layer was etched by using the PS film as a mask. Finally, the dot hollows were filled with PANI using electrolytic polymerization. Electrical modification of the PANI dots pattern was demonstrated using a SPM system in atmosphere. It was demonstrated that the conductive polymer patterned medium can provide reversible single bit recording with 80 nm pitch. This pitch corresponds to the recording density of 100 Gbits/inch^2. It was not easy to define the closed-dots pattern such as the 80 nm pitch on the uniform PANI films in chapter 3 and 4. Therefore, it was seem that the patterned media can prevent the spread of the electrical modified area and crosstalk among neighbor dots, and this method is effective for realizing ultra-high density data storage of conductive polymer recording.

This study is fundamental research on the conductive polymer as a recording media for the scanning multiprobe data storage system. It was demonstrated that the reversible electrical modification of the PANI using SPM. This achievement indicates the conductive polymer has the potentiality for rewritable recording media for the scanning multiprobe data storage system. Then, the high electrical conductance ratio more than 100 was achieved. It was expected that the conductive polymer recording can provide enough signal-to-noise ratio of the conductivity recording. In investigation of repeatability of the conductivity change, the degradation of the PANI was observed. It was considered that this degradation can be improved by optimization of the conductive polymer. Finally, the electrical modification with the smaller dot and pitch sizes was achieved by using the PANI patterned media than that using the uniform PANI films. This achievement indicates that the conductive polymer patterned media have the potential ability to provide the scanning probe ultra-high-density recording. In consequence, this study shows the capability and potential ability of the conductive polymer as the recording media for the scanning multiprobe data storage. In order to achieve ultra-high density recording beyond 1 Tbits/inch^2, it will be required that the optimum design of the conductive polymer and the precision control of the conductive polymer deposition in the synthesis on molecular level.

論文審査結果の要旨

高度情報化社会の進展により、情報記録装置は小型化も併せてより急速な記録密度の向上が求められているが、既存の記録原理に基づいた方法では高密度化に物理的限界が来ると言われている。そこで、1T bits/inch^2 以上の高記録密度を有する次世代の記録方式として、走査型プローブ顕微鏡を利用したマルチプローブ記録システムが検討されている。本論文は、マルチプローブ記録システムのための記録媒体として導電性高分子についての研究成果をまとめたもので、全編 8 章よりなる。

第 1 章は序論であり、本研究の背景および目的を述べている。

第 2 章では、導電性高分子の電気的特性および電導機構について論じ、導電性高分子であるポリアニリンの基本的特性と合成法について有用な知見を述べている。

第 3 章では、スピンコート導電性膜の作製と評価について述べている。このスピンコート導電性膜において、走査型プローブ顕微鏡を用いて導電率を局所的に変化させることに成功している。この成果は、ポリアニリンが記録媒体に使えることを示した重要な成果である。

第 4 章では、自己組織化単分子膜を利用した表面開始重合によるポリアニリン薄膜の成膜と、それに対する電気的修飾実験について述べている。走査型プローブ顕微鏡を用いて、局所的にポリアニリン薄膜の導電性を可逆的に変化させることに成功している。これは、リライタブル記録ができることを示した重要な成果である。

第 5 章では、マイカのへき開面を利用した原子スケールの Au 平坦面を作製し、その表面に表面開始重合法によって均一なポリアニリン薄膜が製膜できることを示し、電気的に記録ができることを示している。これは、実用上重要な成果である。

第 6 章では、電子線リソグラフィによる導電性高分子パターンドメディアの作製について述べ、繰り返し書き込み可能回数について新しい知見を得ている。

第 7 章では、ブロック共重合体リソグラフィを用いたパターンドメディアについて述べている。ポリアニリンドットアレイを形成し、電気的修飾を行った結果、ピッチ 80 nm の記録を達成している。この成果は、ポリアニリンのパターンドメディアがプローブ記録に使えることを示した重要な成果である。

第 8 章は結論である。

以上要するに本論文は、導電性高分子の合成と薄膜の作製および走査型プローブ顕微鏡による電気的修飾実験を行うことによって、マルチプローブ記録システムにおける記録媒体として導電性高分子が有用であることを示している。この成果は、ナノメカニクスおよび情報工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。