学 位 論 文 の 要 旨

銀めっき膜の結晶配向制御に関する研究
（Study on crystalline orientation control of electrodeposited silver film）

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本研究は，車載用スイッチおよびコネクタに使用される銀めっき膜を研究対象として，めっき膜結晶の配向性を制御し，耐熱性，加工性，耐摩耗性などの機械的特性を向上させることを目的とした。

第 1 章では，銀めっき膜は高い導電性や低い接触抵抗などの優れた特性を持ち，そのため，自動車に搭載されるスイッチやコネクタの接点材料に広く用いられている点を述べ，高電圧コネクタや次世代スイッチなどの新たな用途に対する課題点を述べた。

第 2 章では，銀めっき膜において，結晶配向を制御することにより，耐熱性，曲げ加工性の改善が可能であることを示した。高シアン銀めっき液の構成成分および添加剤であるセレンの濃度を調整し，電解条件を制御することにより，めっき膜中の結晶粒の方位を{200}，{111}および{220}に配向させることに成功した。特に，めっき後の再結晶によって得られる{200}優先配向銀めっき膜は，耐熱性と曲げ加工性に優れることを明らかにした。めっき後の再結晶は銀めっき液中のセレン濃度により制御が可能である。本研究のめっき条件では，セレン濃度が 3～20 mg/dm^3 で最適となった。銀めっき液中のセレンは，電解析出時に活性サイトに吸着し結晶粒を微細化することで，めっき成膜時に生じる原子空孔などの点欠陥や転位の生成に影響を及ぼし，再結晶の駆動力となる銀めっき膜の内部応力を上昇させると考えられる。

第 3 章では{200}優先配向銀めっき膜の再結晶挙動の詳細解析を行った。{200}優先配向銀めっき膜は，めっき成膜直後は結晶粒が 5 nm 以下の微細な状態であり，ランダムな結晶配向を示した。再結晶の初期段階においてナノメートル単位の(001)方位結晶粒および(212)方位結晶粒が結晶核として生成する。生成した(001)方位結晶粒が核となり，周辺の結晶粒が 5 nm 以下の微細な領域を蚕食しながら急速に成長する。めっき後，再結晶は 6 時間で完了することを確認した。

第 4 章では銀めっき膜の結晶配向が耐熱性，加工性，耐摩耗性などの各種特性に及ぼす影響について検討した。再結晶により得られる{200}優先配向銀めっき膜は，結晶粒径が大きく，粒界が少ない。また，再結晶により，めっき膜の内部応力が低下しているため，耐熱

環境下でも結晶状態の変化がなく安定している。そのため，高温下においても，銅の拡散経路が少なく，母材からの銅の拡散が抑制されることで，優れた耐熱性を示す。さらに，めっき後再結晶により，銀めっき膜中の点欠陥や転位などの欠陥が減少することで，曲げ加工中の転位の集積が減少すること，また fcc 金属において曲げ加工に優位な集合組織である cube 方位分率が高いことにより，曲げ加工性に優れる。このように{200}優先配向銀めっき膜は，耐熱性と曲げ加工性に優れることにより，今後自動車の電動化により，要求の増加が予想される車載高圧コネクタ向けに適用可能であると考えられる。

第 5 章では，次世代車載スイッチに求められる銀めっき膜の更なる耐摩耗性の向上を目指し，自己潤滑性を有するグラファイトを複合化した銀-グラファイト複合めっき膜の創製を目的とした。酸化処理により，疎水性グラファイト粒子表面を親水性に変化させることで，銀めっき液への分散性を向上させることを可能とした。その結果，カーボン複合化量が 2.0 wt%と従来よりも高い銀-グラファイト複合めっき膜を得ることに成功した。銀めっきの結晶配向とカーボン複合化量には関係があり，銀めっき膜の{220}配向強度比が高い方がカーボン複合化量が増加し，耐摩耗性も向上した。{220}配向強度比が高い場合，銀めっき膜の表面凹凸が大きい析出状態になり，グラファイト粒子の吸着と銀めっき膜への取込みが起こりやすくなったためと考えられる。さらに，めっき液組成を検討し，Ag/KCN 濃度比およびセレン濃度の最適化を図った。その結果，高い電流密度(3 A/dm^2)でも{220}配向強度比を高くすることに成功し，カーボン複合化量の高い(2.24 wt%)銀-グラファイト複合めっき膜を創製し，耐摩耗性と生産性の両立を可能とする手法を構築した。

第 6 章では，本研究を統括した。

In this study, electrodeposited silver films used switches and connectors in automobiles were investigated in terms of controlling the crystalline orientation to improve their mechanical properties, such as electrical contact resistance of the surface after a heating test, bend formability and wear resistance.

In Chapter 1, it was described that electrodeposited silver films have outstanding properties, such as high electrical conductivity and good electrical contact resistance of the surface. Owing to these properties, electrodeposited silver films have been used in many applications, such as contacts in switches and connectors in automobiles. Some problems of electrodeposited silver films were clarified to apply them to new applications, such as the high-current and high-voltage connectors for power devices in hybrid vehicles and electric vehicles and next-generation switches in automobiles.

In Chapter 2, it was shown that heat-resistant and bend formability of electrodeposited silver films can be improved by controlling the crystalline orientation of the film. By optimizing the electrodeposition conditions and the concentration of compositions and Se added as a brightener in high-cyanide silver plating solution, electrodeposited silver films oriented to {200}, {111} and {220} were successfully obtained. Especially, an electrodeposited silver film with high {200} orientation ratio exhibited good electrical contact resistance of the surface after a heating test and had good bend formability. It was clarified that the electrodeposited silver film with high {200} orientation ratio is obtained by self-annealing after electrodeposition, and the self-annealing can be controlled by the concentration of Se in silver plating solution. In this study, the concentration of Se from 3 to 20 mg/dm^3 produced the best results. It was suggested that Se added in silver plating solution had crystal grains of electrodeposited silver film refine by absorbing active site of silver during electrodepositing. The refinement of grains causes to form vacancies and dislocations. Thus internal stress in the electrodeposited silver film increases and it becomes the driving force of recrystallization.

In Chapter 3, the recrystallization phenomena of an electrodeposited silver film with high {200} orientation ratio was investigated in detail. It was confirmed that there are random-oriented fine grains with crystallite sizes of approximately 5 nm or less in an as-electrodeposited silver film with high {200} orientation ratio. In the initial stage of self-annealing, (001) and (212) oriented recrystallized grains with a size of nm order nucleated. Moreover, nucleated (001) oriented grains rapidly grew by encroaching on neighboring fine grains with crystallite sizes of approximately 5 nm or less during storage. When the storage time was more than 6 h, the growth of recrystallized grains was negligible.

In Chapter 4, the effect of the crystalline orientation of the silver films on their properties such as heat-resistant, bend formability and wear resistance was investigated. A preferentially {200}-oriented electrodeposited silver film obtained by recrystallization after electrodeposition had a large grain size and few grain boundaries. Moreover, internal stress in the film was reduced by recrystallization so that the grain size was stable during the heating test. Since the number of grain boundaries allowing the diffusion of Cu during the heating test was reduced and the diffusion of Cu from a matrix was inhibited, the electrical contact resistance of the surface of the film after heating was improved. In addition, when lattice defects such as vacancies and dislocations were decreased by recrystallization after electrodeposition, accumulation of dislocations in the bending was also decreased. Moreover, the ratio of cube-orientation which has a positive effect on bend formability in fcc metals was high in the {200}-oriented electrodeposited silver film. Due to the decrease in accumulation of dislocations and the high ratio of cube-orientation, the bend formability was improved. It is considered that the electrodeposited silver film with high {200} orientation ratio will apply to the high-current and high-voltage connectors for power devices in hybrid vehicles and electric vehicles which are expected to increase in the future.

In Chapter 5, the silver-graphite composite film with self-lubricating was investigated to improve wear resistance of electrodeposited silver film for next-generation switches in automobiles. The dispersion of graphite particles in silver plating solution was improved by the wet oxidation treatment which removed the hydrophobic organic substances on the surface of graphite particles. As the result, the silver-graphite composite film with higher content of carbon (2.0 wt%) was successfully obtained compared to the conventional one. The crystalline orientation in the film affected the content of carbon. When the silver-graphite composite films had higher {220} orientation ratio, they had high content of carbon and their wear resistance were improved. It was confirmed that rough surface texture of electrodeposited silver films with high {220} orientation ratio helped to absorb graphite particles on their surface and to compose these graphite particle into electrodeposited silver films. By optimizing Ag/KCN ratio and the concentration of Se in high-cyanide silver plating solution, the silver-graphite composite film with higher {220} orientation ratio and higher content of carbon (2.24 wt%) was successfully obtained with current density (3 A/dm^2) in electrodeposition. The obtained composite film showed excellent wear resistance.

In Chapter 6, this study was summarized