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Thermal Stability Studies on Copper Thin Films Formed by a Low-Kinetic-Energy Particle Process

Tatsuyiki Saito, Tadahiro Ohmi, Tadashi Shibata
Masahito Otsuki, and Takahisa Nitta(*)

Department of Electronics, Faculty of Engineering
Tohoku University, Sendai 980, Japan

(*) Device Development Center, Hitachi Ltd.,
Ohme, Tokyo 198, Japan

Thermal stability of copper thin films formed on SiO_2 by a low-kinetic-energy particle process has been investigated. Completely (111) oriented Cu films created on SiO_2 by the process are found to transform into almost completely (100) oriented films when subjected to thermal annealing at temperatures greater than 180°C. As the result of such transformation, (100) oriented grains as large as 50~100μm are formed on SiO_2 after thermal annealing at 450°C for 30 min. From these observations, the non-thermal equilibrium nature of the copper thin film growth process by a low-kinetic-energy particle process has been experimentably verified, and a suggestion is made on optimizing the deposition condition for future integrated circuit application.

INTRODUCTION

The establishment of advanced metallization scheme for low-resistivity high reliability interconnect formation is one of the most important issues in realizing future ultra large scale integration. A new metallization scheme utilizing pure copper as an alternative to widely used aluminum or aluminum-based alloys in conjunction with a low-kinetic-energy particle process has been developed.[1,2] Owing to the unique feature of the process, several interesting features of this new metallization scheme have been reported. The determination of crystal structure of a film, such as (100) or (111) orientation is able to be selected by the choice of ion bombardment energy. Ideal Schottky diodes were formed essentially at a room temperature without any alloying heat cycles. Excellent adhesion of Cu films on SiO_2 is also demonstrated[2].

The purpose of this paper is to report on the thermal stability studies carried out on Cu films which were deposited on SiO_2 by the low-kinetic-energy particle process.

EXPERIMENTAL

Copper (Cu) films were grown on thermally oxidized silicon wafers using the rf-dc coupled mode bias sputtering system described in Ref(1-3). Cu film deposition was performed under a back ground pressure of $5x10^{-9}$Torr using a 6N purity target. Typical film formation conditions were the rf power of 40W, the operating Ar gas pressure of $3x10^{-3}$Torr, and the target bias of -400V. Typical film growth rate under this condition was about 0.1μm/min. and approximately 1μm thick films were grown. The substrate bias which determines the energy of ions bombarding the growing film surface was varied from +10 ~ -80V. Thermal annealing of Cu films were carried out in an Ar gas ambient at various temperatures of 140°C ~ 600°C. X-ray diffraction analysis and the reflection electron diffraction analysis were performed to investigate the crystal structure of Cu films before and after the thermal anneal. The surface morphology changes produced by thermal annealing was observed by low-energy (5KeV) scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns obtained from Cu films before and after the thermal anneal at 450°C. The data are shown for two different kinds of samples, viz, the film formed with Vs=0V (a) and that formed with Vs=-80V (b). In the case of Vs=0V sample, the main diffraction peek is (111) and a small (200) peak is also visible. No substantial change occurs by thermal annealing. On the other hand, as deposited film formed at Vs=-80V is a completely (111) oriented film. However, the film has been converted to an almost completely (100) oriented film after thermal annealing.

The dependence of (111) and (200) X-ray diffraction peaks on the substrate bias voltage applied during the film growth is demonstrated in Fig. 2 for both before (a) and after (b) the thermal annealing. In as deposited films, the majority of orientation is (111) indifferent to the substrate bias voltage. It is clearly seen from Fig. 2(b) that in films deposited with substrate voltage greater than -50V, the film orientation is almost completely converted from (111) to (100). In addition, substantial increase in the peak hight is also observed. On the other hand, in samples deposited with substrate bias voltage smaller than -40V the majority of orientation is (111) even after the thermal anneal, although a small increase in the (200) peak hight is observed.

The effect of annealing temperature on such crystal structure transformation is shown in Fig. 3 for Cu films deposited at Vs=-80V. The threshold temperature for the (111) to (100) transformation is found to exist between 140°C ~ 180°C for Cu films deposited at Vs=-80V.

It was pointed out that the concurrent ion bombardment on the growing film surface has an effect of making the (111) plane of the film align normal to the direction of ion bombardment.[1,5] The effect has been interpreted in that only the closed packed surface survive under energetic ion bombardment. This is the reason why as deposited films exhibit an almost complete (111) orientation. However, the most stable film orientation of Cu seems to be (100). In other words, ion-bombardment created (111) oriented films are not thermally stable, thus easily transform into more stable (100) oriented films. If the (111) orientation created by the ion bombardment were the most stable structure of the film, such transformation would not occur. This is the

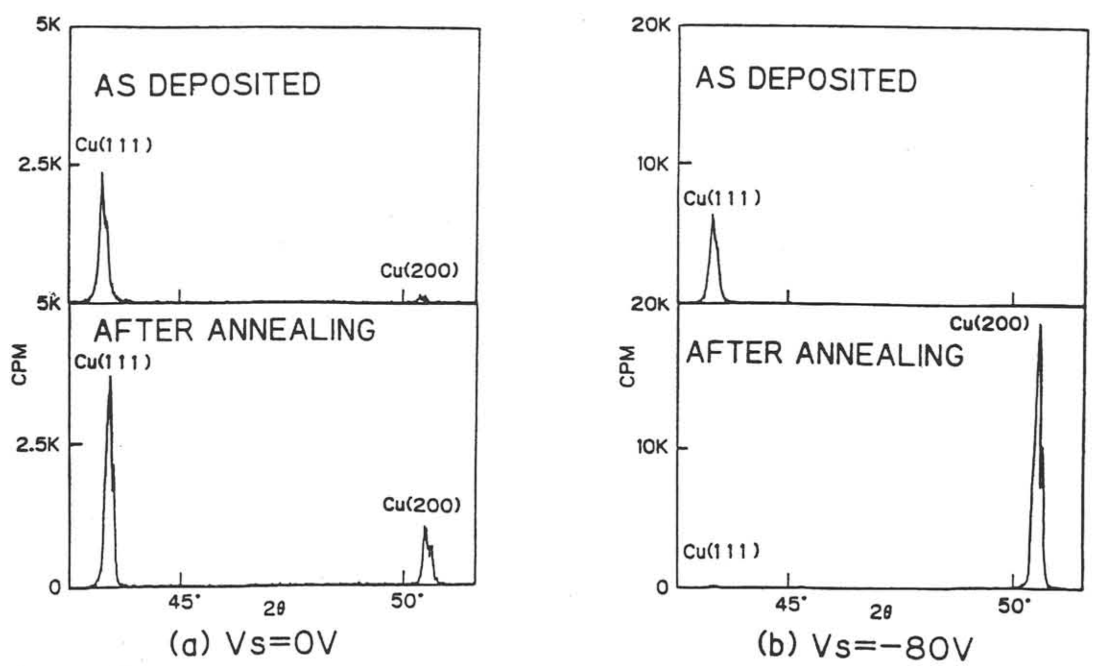

Fig. 1. X-ray diffraction patterns from copper films deposited on SiO_2 with substrate bias voltage of 0V (a) and -80V (b). Thermal annealing was performed in Ar at 450°C for 30 minutes.

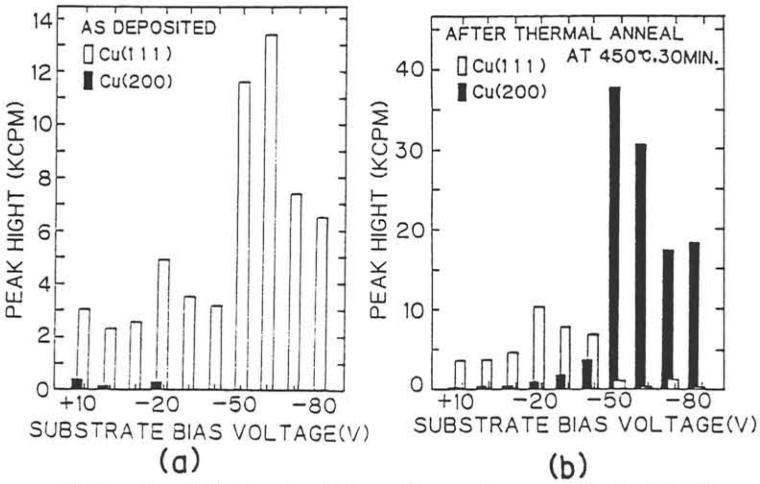

Fig. 2. Substrate bias dependence of Cu(111) and Cu(200) X-ray diffraction peak hights for as deposited films (a) and films annealed at 450°C for 30minutes (b).

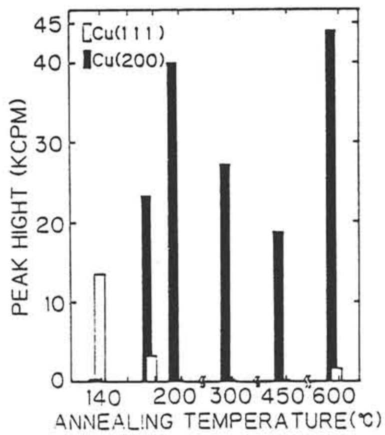

Fig. 3.Cu(111) and Cu(200) X-ray diffraction peak hights as a function of annealing temperature for Vs=-80V samples.

case for aluminum films formed by the same technique(4,7), where only the (111) orientation was observed both in as deposited films and in samples annealed at temperatures up to 500°C.

Surface morphology of Cu films before and after the thermal anneal is shown in Fig. 4 for Cu samples formed at Vs=0V and at -80V. Since as deposited films formed at Vs=0V exhibit a quite smooth mirror surface, we failed to find any surface textures as demonstrated in Fig. 4(a). On the other hand, slightly roughened surface is observed in the Vs=-80V sample (b). A drastic change in the surface morphology after thermal annealing is clearly visible in the figure. In the sample of Vs=0V, a high density net-like pattern appears (c), which was created by grain boundary lines. The average grain size is approximately 1.7μm. Such a surface texture was quite common to all the samples formed at Vs=+10~-40V. Quite interesting to note is the large grain formation observed in the sample of Vs=-80V (d). The net-like pattern becomes very sparse, and most of the grains show grain sizes as large as 50~100μm. From the results of X-ray diffraction analysis presented in Fig. 2(b) as well as by the scanning micro-probe RHEED analysis(6), it is concluded that the large grains shown

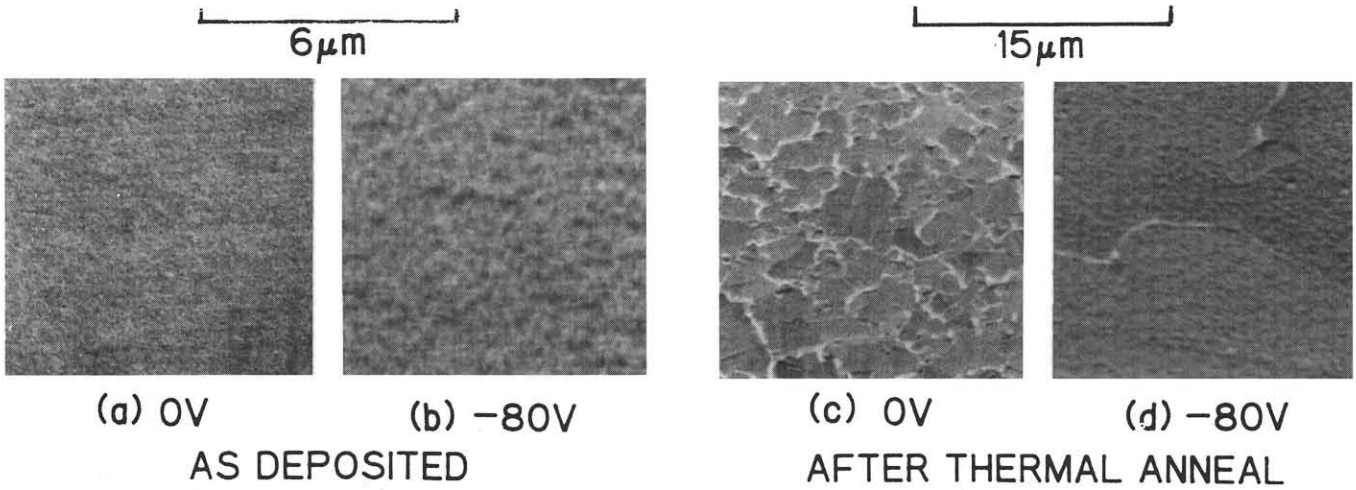

Fig. 4. SEM pictures showing surface morphology in Cu films before and after thermal annealing at 450°C for 30min, for films grown under two different ion bombardment conditions, viz., Vs=0V (a, c) and at Vs=-80V (b, d).

in Fig. 4(d) are (100) oriented crystals. The reflection electron diffraction (RED) analysis of the film of Vs=0V showed only a halo pattern, indicating the formation of a fairly disordered film, while that for the film formed at Vs=-80V showed clear diffraction patterns indicating the formation of a polycrystalline film with a preferred orientation of (111). Judging from the results of RED as well as the small X-ray diffraction peaks shown in Fig. 2(a), as deposited films of Vs=0V would be a fine grain polycrystalline film. Large area of grain boundaries resulted from small grain sizes probably retards the transformation process from (111) to (100) structure. This is the reason why transformation does not occur for Cu films deposited with substrate bias voltage below -40V. Therefore, it is known that ease of crystal structure transformation in Cu films is very much dependent upon the crystal structure of an as deposited film.

Thermal instability in the Cu film structure found in this study is not a desirable effect for practical applications such as interconnect formation for ULSI. Cu film deposition should be performed under the ion bombardment condition that grows the most stable structure, i.e., completely (100) oriented films. This would be realized by the increase in the total energy dose to a growing film surface, in which a sufficient amount of ion flux is supplied while keeping the individual ion bombardment energy low enough not to enhance (111) orientation.

CONCLUSION

The non thermal equibrium nature of the Cu thin film growth process by a low-kinetic-energy particle process has been experimentally verified. Completely (111) oriented Cu films created on SiO_2 by the process are found to transform into almost completely (100) oriented films when subjected to thermal annealing at temperatures greater than 180°C. As the result of such thermal anneal process, (100) oriented grains as large as 50~100μm are formed on SiO_2. The Cu films showing mixed orientation of (100) and (111) in as deposited films do not show any appreciable changes in their crystal orientation. For practical ULSI applications, further studies are needed to form completely (100) oriented structure in as deposited films by optimizing the ion bombardment condition.

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