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Area Selective Aluminum Patterning by Atomic Hydrogen Resist

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We have proposed atomic scale lithographic technology using atomic hydrogen resist. The key features of the atomic hydrogen resist process are (1) patterning of monolayer-thick terminated-H on Si surface by electron beam exposure and (2) selective growth of Al on remaining terminated-H by low-pressure CVD using $(CH_3)_2AlH$ and H_2. In the electron-beam exposed area, the terminated-H on Si is removed and the Si surface is activated. Then the activated Si surface is oxidized in nanometer scale in the cleanroom air environment. The Al is selectively deposited on the remaining terminated-H region. Clear Al pattern has been successfully formed by the atomic hydrogen resist process.

1. Introduction

Atomic scale lithographic technology is strongly required for fabricating future nanometer and atomic scale devices and ULSI's. The new lithographic process should have the capability of relatively high through-put, because giga-order number of devices are integrated on a ULSI chip. In order to improve the resolution of a lithographic process, the resist thickness should be thinned as possible, *i.e.*, ultimately monolayer thickness.

In this paper, we report, for the first time, an ***atomic resist process*** for the future nanometer and atomic scale fabrication technology. The atomic resist in this work is monolayer hydrogen terminated on Si surface. The atomic resist is patterned by an electron beam (EB) lithographic technique. The patterned Al is selectively deposited on the H-terminated surface by low-pressure CVD using DMAH[$(CH_3)_2AlH$] and H_2.[1-4]

2. Atomic Resist Process

Figure 1 shows the new atomic resist process.

(1) **[Atomic resist formation]** A plain Si wafer is chemically cleaned by H_2SO_4:H_2O_2 (4:1) solution, with intermediate rinse in ultrapure water. The wafer is then pretreated by a short dip in HF:H_2O (1:100), followed by an ultrapure water rinse for 10min. After this procedure, the Si surface is mainly terminated by monolayer hydrogen.[5]

(2) **[Electron beam lithography, Fig. 1(a)(b)]** The atomic resist, *i.e.*, terminated-H atom on the Si surface, is removed by electron beam lithography. The Si surface is activated by hydrogen desorption, then the activated Si surface is oxidized in nanometer scale when the Si wafer is carried from the EB machine to the Al CVD apparatus through the cleanroom air environment. The remaining terminated-H area is stable in the air environment.

(3) **[Selective Al deposition, Fig. 1(c)]** Aluminum is selectively deposited on the H-terminated area by LP-CVD using $(CH_3)_2AlH$ and H_2 at 270°C.

(4) **[Area selective Al patterning, Fig. 1(d)]** Patterned Al is formed on the H-terminated area automatically.

The key features of the atomic resist process are (1) pattering of monolayer-thick terminated-H on Si surface and (2) selective Al deposition on H-terminated Si surface. The terminated-H in this process plays efficiently not only as a resist but also as a reactive species which reacts with CH_3-radical of DMAH molecule.

Surface Electrochemical Reaction for Selective Al Growth

One of the key features of the atomic resist process is selective Al CVD on H-terminated Si surface.[1-4] We have found that the aluminum is selectively deposited on electrically conductive material such as n-Si, p-Si, Ti, TiN, *etc.* and is not deposited on electrically insulating material such as SiO_2, PSG, BPSG, SiN, *etc.* 0.3μmϕ deep-submicron via-holes with aspect ratio more than 3 have been completely filled with the selective Al. The Al deposited on Si surface is single

crystal: Crystal orientation relationships are (100)Al on (111)Si and (111)Al on (100)Si.

For the selective Al growth on Si wafer, we have proposed the surface electrochemical reaction model.

The most significant point of this model is (1) catalytic contribution of surface free-electrons, (2) surface terminated-H atom and (3) selective reaction between the terminated-H atom and CH_3-radical.

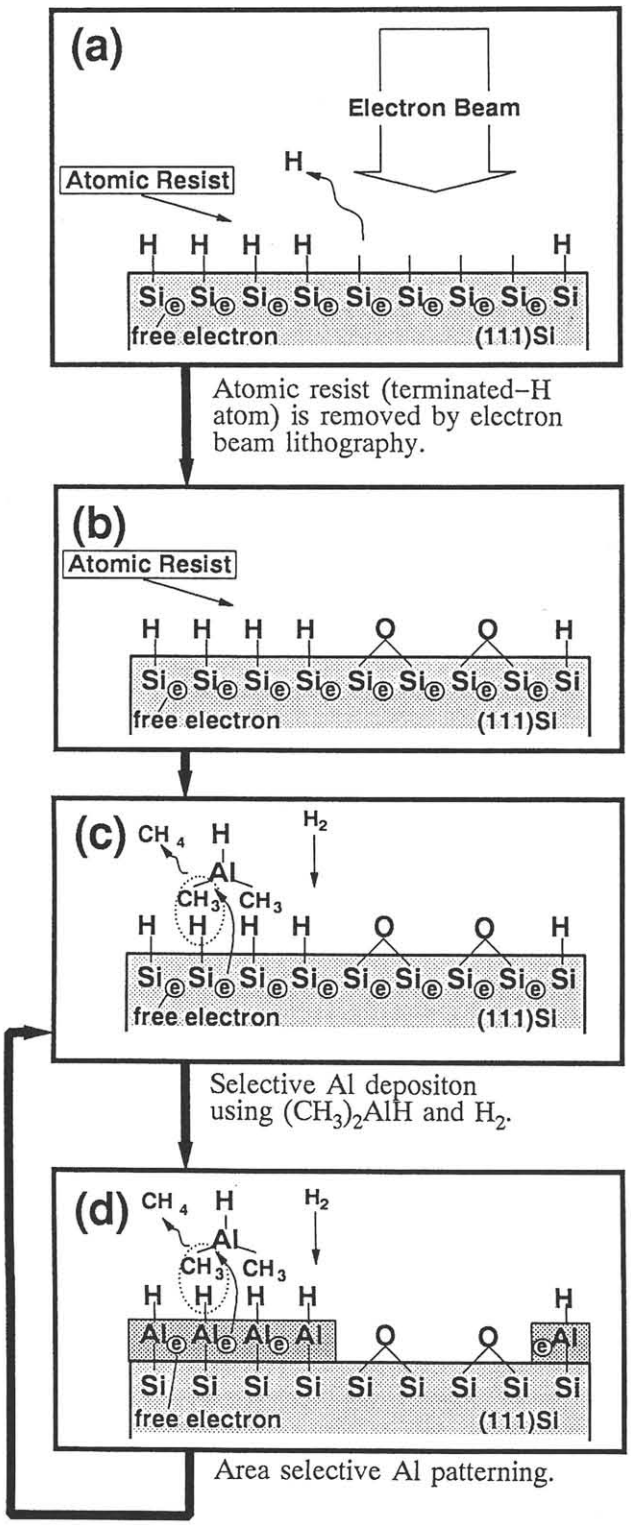

Fig. 1. Atomic Resist Process

At first, the (111)Si surface is mainly terminated by H atom after the diluted-HF dip followed by pure water rinse. The Si surface is considered to be mainly terminated by monohydride. Since terminated monohydride is considered to be desorbed 535°C[6], the Si surface remains to be terminated by hydrogen at the growth temperature of 270°C. When the DMAH molecule adsorbs on the H-terminated Si surface as shown in Fig. 1(c), Al-CH_3 bond is weakened (or dissociated) because of the catalytic contribution of free-electrons. Then CH_3-radical of the DMAH reacts with the terminated-H atom to produce volatile CH_4 molecule; $CH_3+H\rightarrow CH_4$. Thus, Al is deposited on Si surface (Figs. 1(c)(d)). It is well known that the reaction of $CH_3+H\rightarrow CH_4$ is inherently an active reaction and the activation energy of this reaction is very small. The reaction rate of $CH_3+H\rightarrow CH_4$ is one order larger than that of $CH_3+CH_3\rightarrow C_2H_6$[7], so that the reaction of $CH_3+H\rightarrow CH_4$ is able to occur selectively.

Because the bonding energy of Al-H is larger than that of Al-CH_3[8], Al-H remains after depositing Al, *i.e.*, the H atom remains on the newly deposited Al surface as a new terminated-H atom. The overall reaction for DMAH to produce Al requires additional H atom. The additional terminated-H atom is supplied by the dissociation of H_2 molecule because of the catalytic contribution of surface free-electrons at the heated metal surface. At the Al surface, there exist the free-electrons which contribute to the reaction and the terminated-H atom remains. The terminated-H atom on the surface reacts repeatedly with CH_3-radical to deposit Al as shown in Figs. 1(c)(d).

For the reaction on SiO_2 or on nanometer-thick oxidized Si surface, there is neither terminated-H atom nor free-electron which can catalytically contribute to the reaction. H_2 molecules can not be dissociated to supply the terminated-H atom if the H_2 molecules are supplied to the SiO_2 surface. The reaction of $CH_3+H\rightarrow CH_4$ dose not occur on SiO_2, so that Al is not deposited on SiO_2.

The catalytic contribution of surface free-electrons has been confirmed by our experimental results[1-4]: (1) the Al is selectively deposited on the electrically conductive materials such as Si, Ti, TiN, *etc.* and not deposited on electrically insulating materials such as SiO_2, PSG, BPSG, etc., (2) the nucleation density on n-Si at the initial growth stage is larger than that on p-Si, and (3) the Al is deposited on the insulating materials when free-electrons are supplied from the rf plasma.

The crystal quality of single-crystal Al on Si has been deteriorated on the intentionally incomplete H-terminated condition, which is varied by changing the rinsing duration after the dilute HF-dip or by baking the H-terminated Si above 350°C prior to Al deposition.[3] Thus, the terminated-H on Si has been confirmed to play an important role in the selective Al growth.

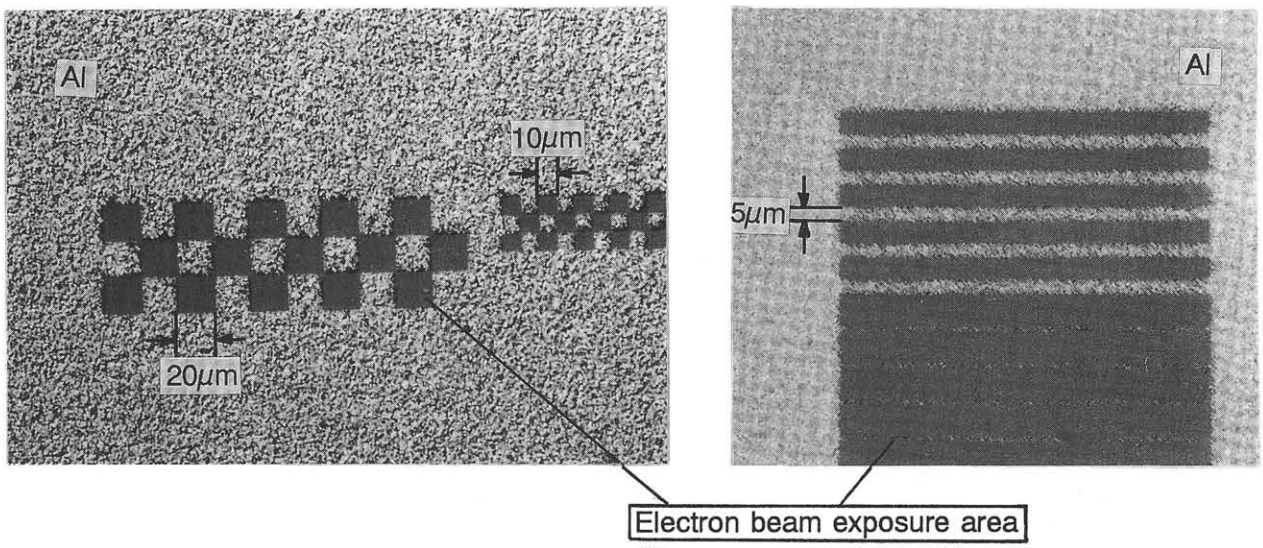

Fig. 2. Aluminum patterning by atomic hydrogen resist.

3. Area Selective Al Patterning

Figure 2 shows Nomarski micrographs of patterned Al by the atomic resist process.

The wafer used was an n-type, 1-2Ωcm, (111)-oriented Si. In the electron beam lithographic procedure, the commercial EB machine (JEOL, JBX-5DII/U) was used. The acceleration voltage was 25kV. The electron dose was 9×10^{17}electrons/cm^2. Aluminum was deposited at 270°C. Total pressure and DMAH partial pressure were 1.2 Torr and 3×10^{-3} Torr, respectively. The aluminum thickness was 4000Å.

Clear Al pattern was formed by the atomic resist process. Aluminum was formed on the H-terminated area, while even Al nucleus was not formed on the EB exposure area. Clear Al patterning as shown in Fig. 2 was observed when the electron dose was larger than 3×10^{16}electrons/cm^2. Instead of electron beam, clear Al pattern was also formed using O_2^+ or Ar^+ ion beam. In the case of O_2^+ ion beam exposure, clear Al patterned was formed when the ion dose was 3×10^{14}ions/cm^2 at 15kV.

Since the atomic resist thickness is monolayer order and the minimum electron beam diameter of the EB machine used is 80Å, the atomic resist process has a potential being used for fabricating atomic and nanometer scale devices such as single electron transistor[9], in which 300Å-order ultrafine patterning is required.

4. Summary

We have, for the first time, successfully formed area selective Al patterning by the atomic hydrogen resist. The key features of the atomic hydrogen resist process are (1) patterning of monolayer-thick terminated-H on Si surface by electron beam exposure and (2) selective Al growth on the remaining terminated-H region. The atomic resist process has a potential being used for the future atomic and nanometer scale devices and ULSI process.

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