Electroless Metallization of Silicon Using Metal Nanoparticles as Catalysts and Binding-Points

Masato Enomoto[1)], Shinji Yae[1)], Hiroyuki Atsushiba[1)], Naoki Fukumuro[1)], Susumu Sakamoto[1,2)], and Hitoshi Matsuda[1)]

[1)] Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo 2167 Shosha, Himeji, Hyogo 671-2280, Japan

[2)] Nippon Oikos Co., Ltd., 3-6-16 Mitsusadadai, Yahatanishi, Kitakyushu, Fukuoka 807-0805, Japan

Surface metallization of silicon (Si), that is, adhesive metal-film formation on Si is important for obtaining infallible electrical contacts in various devices, such as solar cells and power devices. Autocatalytic electroless deposition, which is a conventional method to metalize nonmetallic substrates, has several advantages including simplicity of process, uniformity of films, and the covering of complicated structures. This deposition requires surface activation (catalyzation pretreatment) of nonmetallic substrates, generally using tin and palladium (1). It is difficult to obtain adhesive metal films on Si substrates with conventional catalyzation pretreatments. We have recently developed two novel surface-activation processes for the direct electroless deposition of adhesive metal films on Si substrates. One consists of three steps shown in Fig. 1(2,3): Step 1) metal nanoparticle formation by electroless displacement deposition (4); Step 2) Si nanopore formation by metal-assisted hydrofluoric acid (HF) etching; and Step 3) metal filling in nanopores and metal-film formation on the Si surface by autocatalytic electroless deposition. Metal nanorods formed in the Si nanopores work as nanoanchors of metal film on Si. The other novel process uses gold (Au) nanoparticles as catalysts to metalize Si. This Au-nanoparticle process requires no nanopore formation of the step 2 of the former three-step process, and can form fine metal patterns on the Si substrates (Fig. 2).

At the first step of the three-step process, silver nanoparticles, a few tens of nm in diameter and ca. 10^{11} cm^{-2} in particle density, were deposited on a p-Si substrate by immersing the substrate in metal salt solution containing HF. At the second step, Si nanopores were prepared by immersing the Ag-particle-deposited Si substrate in a HF aqueous solution under dark conditions. At the third step, a nickel-boron (Ni-B) alloy film was formed on the Si substrate by using dimethylamineborane as a reducing agent. In the Si metalizing process using Au nanoparticles, the nanoparticles were deposited by the same displacement deposition at the first step, the second step of nanopore formation was omitted, and nickel-phosphorous (Ni-P) films were formed on the Si substrates by using phosphinate as a reducing agent. The adhesion of the electrolessly deposited metal films on Si substrates was examined by a tape test based on Japanese Industrial Standard JIS H8504 corresponding to ISO 2819.

Both processes produced continuous bright metal films on Si substrates. The adhesion of metal films deposited by the three-step process was higher than that of the Au-nanoparticle process, and increased as the Ag nanoparticle size and Si nanopore depth enlarged. The diameter of Si nanopores formed by metal assisted HF etching is almost same as the size of metal nanopartilces used as catalysts. The autocatalytic electroless deposition of metal is initiated by the catalytic metal nanoparticles remaining on the bottom of nanopores. Thus, Si nanopores are fully filled with metal, and the size of metal nanoparticles corresponds to the diameter of metal nanorods. The enlargement of the diameter increases the strength of the nanorods, which work as the nanoanchors, and then improve the adhesion of metal films on Si.

The adhesion of metal films formed by the Au-nanoparticle process increased and then decreased as the Au nanoparticle size enlarged. This can be explained by a binding mechanism of metal coatings based on the low temperature reaction at Si-Au contacts (5).

ACKNOWLEDGEMENTS

The present work was partly supported by Grant-in-Aid for Scientific Research(C) (23560875) from JSPS and A-STEP from JST.

REFERENCES

1. M. Paunovic and M. Schlesinger, Fundamentals of Electrochemical Deposition, 2nd ed., Wiley, NY (2006).
2. S. Yae, T. Hirano, T. Matsuda, N. Fukumuro, and H. Matsuda, *Appl. Surf. Sci.*, **255**, 4670 (2009).
3. S. Yae, K. Sakabe, N. Fukumuro, S. Sakamoto, and H. Matsuda, *J. Electrochem. Soc.*, **158**, D573 (2011).
4. S. Yae, N. Nasu, K. Matsumoto, T. Hagihara, N. Fukumuro, and H. Matsuda, *Electrochimica Acta*, **53**, 35 (2007).
5. A. Hiraki, *Jpn. J. Appl. Phys.*, **22**, 549 (1983).

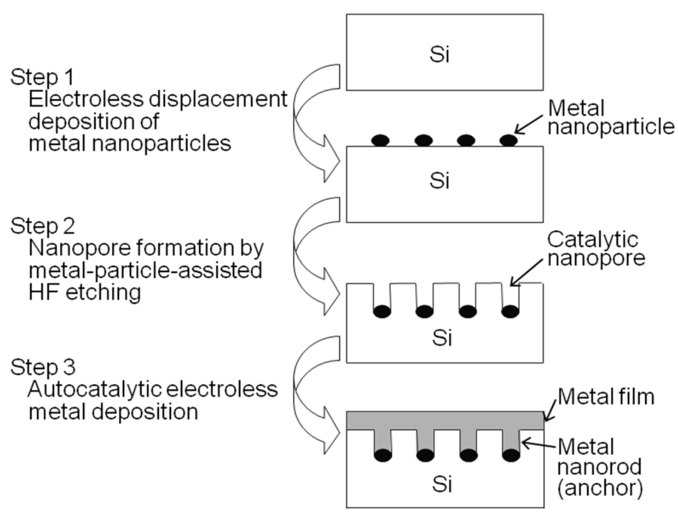

Fig. 1 Schematic process flow of three-step process of electroless metal film deposition on Si substrate using catalytic nanopores (nanoanchors).

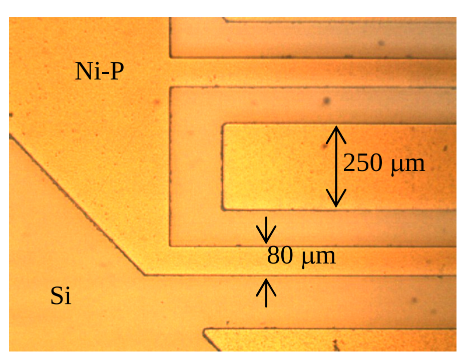

Fig. 2 Metal pattern on Si substrate produced by using Au-nanoparticle process.