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Resist nano-modification technology for enhancing the lithography and etching performance

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Abstract

The fullerene molecules (i.e., C60 and C70) were incorporated in the SUMITOMO NEB-22 negative electron beam resist to investigate the lithographic and etching performances of the resist. The sensitivity, process window and contrast of the modified resist were found to be improved, while the dilution of resist degraded the sensitivity. The electron beam dose affected the designed line width, and the adulterated resist could print sub-50 nm pattern without the problem of line edge roughness. The etching selectivity of gas (CHF_3/CF_4) on silicon dioxide and resist, and gas (Cl_2/O_2) on poly-silicon and resist were evaluated. We found the small amount (0.01–0.02% w/v) of fullerene molecules very effectively promoted the etch resistance and selectivity. The fullerene-incorporated resist was used to pattern self-aligned metal silicides, and nickel silicide on poly-silicon exhibited lower sheet resistance.
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Keywords: Fullerene molecule; Electron beam resist; Etching; Metal silicide

1. Introduction

During the past two decades, there has been an extremely rapid growth in both the technology and the application of microelectronics, to the point that it now pervades virtually all aspects of commercial and military business. The size and performance of microelectronic devices has been improved substantially, especially in the past few years [1,2]. The electron beam direct writing (EBDW), in comparison with optical lithography, is a promising means for controlling and patterning small features, down to sub-100 nm [3]. This technology has a cost advantage for production volumes below 100 lots in the future [3]. In EBDW, the Gaussian beam has better resolution than shaped beam. But, the shaped beam has an at least 10-fold higher throughput than Gaussian beam due to imposing several pixels per shot [4]. In order to achieve the better resolution and high

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throughput for shaped beam technology, the utilization of thin resist film is inevitable [5]. However, the thin resist will face the challenge of poor etching resistance and serious line edge roughness.

Nano-scale molecules are a possible means to solve the problem of low etching resistance and enhance the lithographic performance for the thin resist film generation. The molecules can be incorporated into the resist to alter its performance. Fullerene molecules possess the advantage of being extremely small and monodispersed. Ishii et al. [6] have used fullerene molecule (i.e., 5 wt% C60) to modify positive tone resist, and found the fullerene can enhance the etching resistance and not alter the sensitivity. In addition, they claim the negative tone chemically amplified resist incorporated with 3 wt% C60 exhibits strong environmental stabilization in postexposure delay. In the latter report [7], they find the resist sensitivity is degraded by the C60 due to the dissolution-inhibiting effect. Dentinger and Taylor [8] spike 7.9 wt% C60 into poly(methylmethacrylate) resist, and the etching resistance is promoted 8% and 26% for CF_4 and Cl_2 plasmas, respectively. However, the use of 3–7.9 wt% C60 in the resists and the deterioration of resist sensitivity elevate the fabrication cost and restrict the further application of this technology.

In this study, the sensitivity curve of resists after spiking with C60 and C70 molecules are investigated. The film stress, etch resistance and the effect of shaped electron beam dose on the line width are also evaluated. In addition, we evaluate the electrical property of self-aligned silicide gates by using the C60-incorporated resist.

2. Experimental

The fullerene molecules of C60 and C70 were purchased from Alfa Aesar Company. The toluene solvent was obtained from E. Merck (Darmstadt, Germany). The negative NEB-22 resist used in this study was obtained from SUMITOMO Chemical Co., Ltd. (Japan). The resist samples in this study have four types, named NEB, NEB + Toluene, NEB + C60 and NEB + C70, respectively. The NEB means the NEB-22 resist without any modification. The "NEB + Toluene" means the mixture of 50 ml NEB-22 resist and 50 ml toluene solvent. For the "NEB + C60-0.01%" sample, the 0.01 g C60 fullerene is first dissolved in 50 ml toluene, and then mixes with 50 ml NEB-22 resist. The final concentration of C60 molecule in the resist is 0.01% w/v. In the same manner, the "NEB + C70-0.02%" uses 0.02 g C70 fullerene to prepare the sample.

Electron beam exposure was performed on a Leica Weprint 200 stepper. The electron beam energy was 40 keV, and the beam size was 20 nm. The developer for the electron beam resist was an aqueous 2.38% tetramethylammonium hydroxide (TMAH) solution. A negative-tone electron beam resist was spin-coated on a silicon wafer (150 mm diameter) and baked at 110 °C for 120 s. The thickness of the resist film was ca. 230 nm. After exposure and a post-exposure bake (105 °C for 120 s), the wafer was developed using the TMAH solution. Again, a hard-bake was applied to the wafer (110 °C for 120 s). Critical dimensions were evaluated using either an in-line scanning electron microscope (SEM, Hitachi S-6280) or a cross-sectional SEM (Hitachi S-4000). The stress of resist film was measured by TENCOR FLX-2320 instrument. In the stress measurement, the curvatures of bare silicon wafers, resist-coated wafers were determined.

Silicon dioxide and poly-Si films were etched using a reactive-ion etcher (RIE, Tokyo Electron Limited, Model TE5000, Japan) and an electron cyclotron resonance (ECR) etcher (Anelva ECR-6001, Japan). In silicon dioxide etching, the step 1: 0.2 Torr, 0 W RF, 400 $cm^3\ min^{-1}$ Ar, $CHF_3 + CF_4 = 40\ cm^3\ min^{-1}$, and step 2: 0.2 Torr, 500 W RF, 400 $cm^3\ min^{-1}$ Ar, $CHF_3 + CF_4 = 40\ cm^3\ min^{-1}$. In poly-Si etching, the step 1: 3×10^{-3} Torr, 0 W source microwave, 0 W back RF, $Cl_2 + O_2 = 50\ cm^3\ min^{-1}$, and step 2:$3 \times 10^{-3}$ Torr, 250 W source microwave, 90 W back RF, $Cl_2 + O_2 = 50\ cm^3\ min^{-1}$.

The polysilicon gates with spacer were fabricated with the 0.01% w/v C60-incorporated resist on 6 in. silicon wafer. First, the gate oxide was grown under dry O_2 at 900 °C in quartz reactor to a thickness of 1.5 nm. After a 50 nm poly-Si film was deposited by low pressure chemical vapor

deposition system (LPCVD) and doped by ion implantation, and then patterned to form a gate. The poly-SiGe is also deposited by LPCVD. A 50 nm tetraethyl orthosilicate film was also deposited by LPCVD. The gate spacer was formed by reactive ion etching. To remove native oxide before cobalt deposition, all wafers were dipped in the HF solution. The 5 nm cobalt was deposited by physical vapor deposition system (PVD). The first annealing step for the cobalt silicide ($CoSi_2$) formation was operated at 550 °C in N_2 ambient for 30 s. The un-reacted cobalt was removed by selective wet etching with a mixture of H_2SO_4 and H_2O_2. The second step annealing step was performed at 750 °C in N_2 ambient for 30 s. For the nickel silicide (NiSi) formation, the wafer was deposited 5 nm Ni by PVD. The annealing step used only one step for the sample was operated at 500 °C in N_2 ambient for 30 s. The un-reacted Ni was also removed by wet etching in a mixture of H_2SO_4 and H_2O_2.

3. Results and discussion

3.1. Enhancement of lithographic performance

In the electron beam writing technology, negative tone resist is usually used to fabricate line or low density patterns, especially for the gate line. In this study, the commercial NEB-22 resist is a negative type, and the fullerene molecules such as C60 and C70 are incorporated into the commercial resist. Fig. 1 depicts the resist sensitivity curve. The dose (D_C) for the "NEB" sample that the polymer constituent begins cross-linkage is 5.2 μC/cm^2, while the dose (D_O) that the polymer can achieve 100% cross-linkage is 6.2 μC/cm^2. As to the "NEB + Toluene" sample, both the D_C and D_O are increased. This observation is attributed to the dilution of acid generator in the sample, and therefore, reduces the sensitivity. Interestingly, the sensitivity for 0.01% w/v "NEB + C60" or "NEB + C70" sample is significantly enhanced after nano-material modification. Both the D_C and D_O are decreased to 4.6 and 5.4 μC/cm^2, respectively. This finding suggests that the incorporation of fullerene molecules into resist can

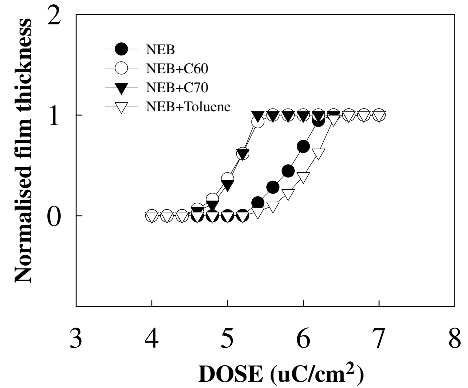

Fig. 1. The sensitivity curves for various resists.

effectively enhance the process throughput. What happens to the decrease of addressing dose for the resist after spiking with fullerene molecules? In the resist, the electron beam activates the bond of acid generator to produce acid, and the acid induces the cross-linkage reaction of the polymer. We infer the fullerene molecules with the tiny size of 0.7–0.8 nm are easily incorporated into the void of resist sample (in Fig. 2). The C60 or C70 fullerene in the void has a better electron affinity ~2.6 eV, and therefore, facilitate the bond activation for the acid generator. As we know the electron accelerating voltage can influence the

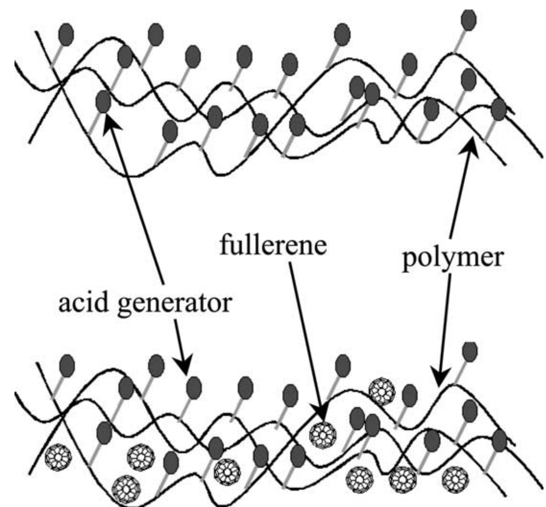

Fig. 2. The model for incorporation of fullerene molecules in the void of resist polymer.

sensitivity, the higher accelerating voltage can improve the resist resolution but deteriorate the resist sensitivity [9]. However, the application of fullerene nano-material can recover the resist sensitivity and enhance the resist throughput.

Fig. 3 indicates the line width increases with the exposure dose. We define the dose range for the "nominal line ± (10%)(nominal line)" as the process window. Table 1 suggests the fullerene-incorporated resist has wider dose window than unadulterated resist. The resist with C60 modification in Fig. 3 can fabricate sub-50 nm line with respect to C70. This phenomenon implies the C60 with smaller size is better for the resist void filling. The SEM images for the resist with 0.02% w/v fullerene modification are illustrated in Fig. 4. The print of sub-50 nm lines can not achieve from Fig. 4(a). The line without fullerene tends to pattern collapse at aspect ratio of 5.75 due to the insufficient adhesion at interface. Fig. 4(b) demonstrates the resist without fullerene can resolve 53 nm lines at aspect ratio of 4.3, but the line has serious line edge roughness problem. The line edge roughness can lead to higher leakage current for the future nano-devices. However, the resist with 0.02% C60 modification can print 46 nm lines (Fig. 4(c)), and 0.02% C70 can print 51 nm lines (Fig. 4(d)). The problem of line edge roughness is not seen for the resist with fullerene modification. This observation is dependent on the void of resist polymer of which is filled with fullerene. The fullerene on the sidewall also can minimize the extent of protrusion of polymer. In addition, the interfacial adhesion between fullerene-incorporated resist and the substrate is stronger than the unadulterated resist and the substrate. The stress for various fullerene-incorporated films is demonstrated in Fig. 5. The resist film without spiking fullerene has large tensile stress (∼2.4 GPa). The spiking of fullerene molecules such as C60 or C70 can prevent the stress, and is beneficial for the surface flatness. The fullerene molecules can fill the void of resist and minimize the deformation as spin-coating the resist.

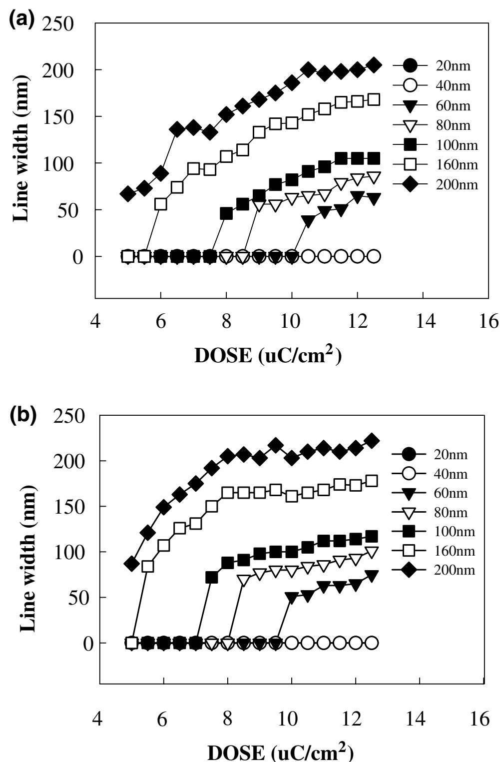

Fig. 3. The effect of electron beam dose on the line width for various designed lines: (a) NEB resist with 0.02% w/v C60; (b) NEB resist with 0.02% w/v C70.

3.2. Enhancement of etching performance

In this study, we use RIE to evaluate the etching resistance for the fullerene-incorporated resist on a silicon dioxide layer. The feeding gas is a mixture of Ar, CHF_3 and CF_4. The etching rates of these resists and the oxide film both decrease upon increasing the CHF_3 content. This observation explains the role CHF_3 in the plasma. The species generated from CHF_3 in the plasma are H^+ and CF_3^-, and the CF_3^- species can quench the activity of CF_3^+ in the plasma. Hence, the etching rate decreases. Fig. 6(a) depicts the etching selectivity for these resists. The selectivity gradually increases upon increasing the relative CHF_3 content. In addition, the increase of amount of fullerene molecules can also enhance the selectivity over that of the unadulterated resist. This observation supports the assumption that the fullerene molecules can effectively fill the free volume of

Table 1
The dose and process window for the resists to print various designed lines

	NEB	NEB with 0.02% C60	NEB with 0.02% C70
Dose for 100 nm line (μC/cm^2)	14	12	11.5
Dose for 80 nm line (μC/cm^2)	14	12	11.5
Dose for 60 nm line (μC/cm^2)	14.5	12.5	11.5
Dose for 40 nm line (μC/cm^2)	Not print	18	17
Process window for 60 nm line (μC/cm^2)	1.5	2	2

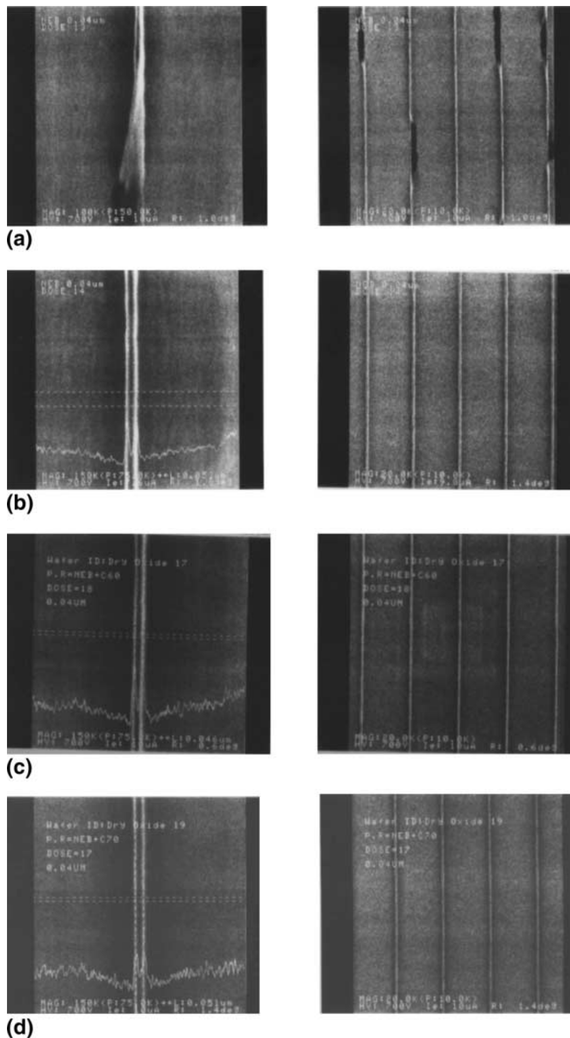

Fig. 4. Top-down SEM images of resist: (a) the sub-50 nm line without fullerene modification; (b) the 53 nm line without fullerene modification; (c) the 46 nm line with 0.02% C60 modification; (d) the 51 nm line with 0.02% C70 modification.

the resist film. The fullerene molecules consolidate the film, and therefore, the resist film is more resistance to the etching gases. We also find the incorporation of C70 has better etch resistance than C60. This finding is attributed to the higher molecular of C70. It should be noted that the amount of fullerene spiking is only 0.01–0.02%, and is much lower than literature [6–8] report (i.e., 3–50%).

The etching behavior of these resists on the polysilicon film is evaluated using an ECR etcher. The feeding gas is a mixture of Cl_2 and O_2. The etch rate of these resists decrease upon increasing the amount of Cl_2. This observation can be explained by considering the relative amount of O_2 in the plasma: a decrease in O_2 ratio decreases its reaction with the carbon-based ingredients of the resist. For the poly-Si film, the etching rate is very small as if the Cl_2 ratio is below 0.8. However, it increases abruptly at the ratio higher than 0.8. This finding indicates that an O_2 ratio greater than 0.2 is required to oxidize the poly-Si film quickly. The silicon dioxide that forms is resistant to Cl_2 etching. Fig. 6(b) depicts the etching selectivity for these resists. The selectivity significantly increases upon increasing the Cl_2 to higher than 0.8. In addition, the increase of amount of fullerene molecules can also enhance the selectivity than the unadulterated resist. This observation also strengthens the role of fullerene molecules mentioned early.

3.3. Application of fullerene-incorporated resists for nano-silicide gate and the electrical properties

The various metal silicided lines, such as self-aligned cobalt silicide ($CoSi_2$)/poly-Si, nickel

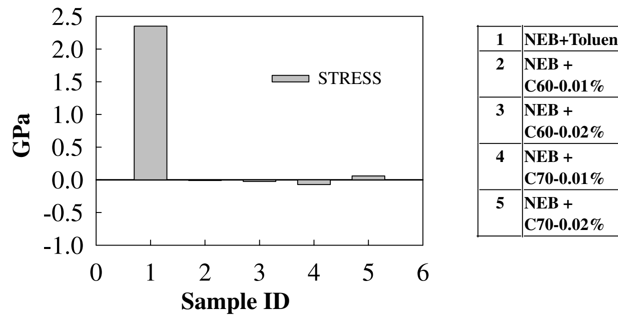

Fig. 5. The stress of resist film on the silicon wafer.

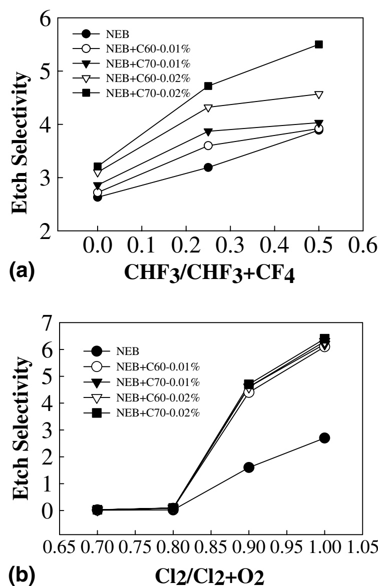

Fig. 6. Etching selectivity of resist with respect to: (a) silicon dioxide; (b) polysilicon.

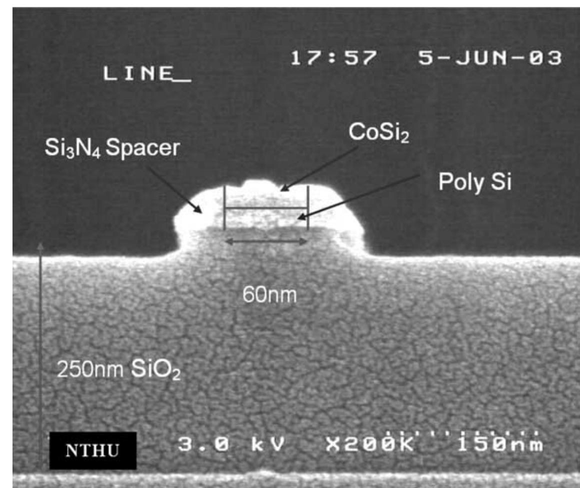

Fig. 7. The cross-sectional SEM image of 60 nm cobalt silicide line.

silicide (NiSi)/poly-Si, and NiSi/poly-SiGe, are fabricated with the 0.01% w/v C60-incorporated resist. The cross-sectional SEM image of 60 nm cobalt silicide line is depicted in Fig. 7. The silicon nitride spacer, self-aligned cobalt silicide, poly-Si and the underlying silicon dioxide layer are successfully fabricated in the Kelvin structure. Then, the sheet resistance (in unit of Ω/sq) of the designed line is determined at a probe station. Fig. 8(a) illustrates the sheet resistance of $CoSi_2$ has no significant difference in the range 100–200 nm. However, the resistance increases dramatically as the line narrowing than 100 nm. The phenomenon has been reported to be linked with the presence of infrequent voids in narrow silicide lines [10]. As to the NiSi/poly-Si line in Fig. 8(b), the sheet resistance gradually decreases with narrowing the line from 200 to 60 nm. By comparison to the effect seen in Co, this behavior has been termed "reversed fine line effect" [10]. This decrease in resistance is explained through an increase in the reaction volume of Ni and Si close to line edges. The sheet resistance of NiSi/poly-Si is much lower than $CoSi_2$/poly-Si. This observation is attributed to the lower Si content in the NiSi than in the $CoSi_2$. The underlying poly-Si of NiSi was changed to poly-SiGe for

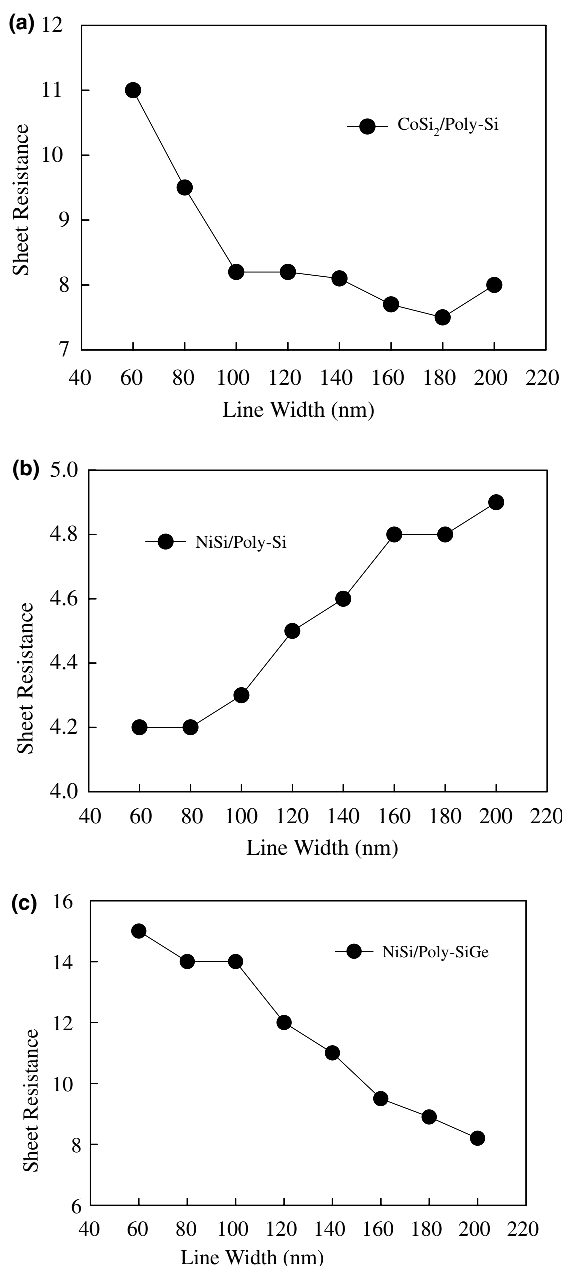

Fig. 8. Sheet resistance of: (a) $CoSi_2$ on polysilicon; (b) NiSi on polysilicon; (c) NiSi on poly-SiGe.

evaluating the electrical property. Fig. 8(c) demonstrates the sheet resistance gradually increases with shrinking the line width. In addition, the electrical property of NiSi on poly-SiGe is deteriorated than on the poly-Si. We suppose the NiSiGe film is formed between the NiSi and poly-SiGe, and has lower Ni percentage.

4. Conclusions

We have established a successful fabrication technique that incorporated the small amount of fullerene molecules in the resist for preparing sub-50 nm lines by electron beam lithography. The improvement of throughput is attributed to the better electron affinity of the fullerene. The prevention of line edge roughness and pattern collapse is also an advantage of this modification technology. In addition, the technique significantly enhances the etching selectivity of resist for plasma gases of CHF_3/CF_4 or Cl_2/O_2. We have used this resist to fabricate various metal silicide gates, and the NiSi on poly-Si has better electrical performance.

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