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Low-energy electron-beam lithography using calixarene

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Low-energy electron-beam lithography using calixarene as a negative electron resist has been investigated in the energy range between 0.5 and 20 keV. The suitability of electron energies down to 2 keV with a writing resolution of about 10 nm is clearly demonstrated. At low electron energies the required electron dose is drastically reduced. Moreover, irradiation damage during the exposure of a high-mobility two-dimensional electron gas using calixarene plays no significant role in the low-energy regime. © *1999 American Vacuum Society.* [S0734-211X(99)00804-5]

I. INTRODUCTION

Low-energy electron-beam lithography in the range of 1–10 keV offers significant advantages over the use of high electron energies for the exposure of sensitive positive electron resists such as PMMA. Since the penetration depth of electrons is smaller for lower energies the proximity effect is strongly suppressed due to a reduction in the number of backscattered electrons from the substrate.[1] The majority of the electrons are inelastically scattered in the resist film and it is their spatial range which limits the lateral resolution. Furthermore, the irradiation damage of the underlying substrate is substantially lower, making low-energy electron-beam lithography an attractive prospect for lateral structuring of high-mobility semiconductor devices.

Recently Fujita *et al.* investigated a new high-resolution negative resist called calixarene.[2–4] Because this resist has a low sensitivity, it is especially important to use low electron energies. Reducing the electron energy will significantly reduce the electron dose required for exposure as is immediately seen using a simplified Bethe equation where x denotes the distance from the sample surface and $W(x)$ the electron energy:[5]

$$dW(x)/dx \sim -1/W(x). \tag{1}$$

Moreover, in the case of negative resists the electron beam usually exposes the active area of the defined device structure so reducing the electron energy is important for the elimination of radiation damage. Low-energy electron-beam lithography on high-resolution negative electron resists is therefore especially well suited for defining nanostructures such as single-electron tunneling transistors.[6]

Here, we investigate the exposure parameters of a calixarene resist at electron energies down to 0.5 keV. We determine both the resolution of the resist as well as the radiation damage of a high electron mobility transistor (HEMT) structure in the energy range between 1 and 20 keV. In addition we investigate the differences in the exposure parameters of nanometer scale and large scale structures caused by proximity effects.

II. EXPERIMENTS

A. Exposure parameters

In order to study the influence of the electron energy on the exposure dose, writing resolution and proximity effects of the calixarene resist hexaacetate *p*-methylcalixarene (MC6AOAc), various silicon samples were coated with a thin calixarene film (~40–50 nm). These films were prebaked at 170 °C for 30 min and then exposed at different electron energies and electron doses. After exposure, the samples were developed for 30 s in xylene and the development was then stopped by immersion for 30 s in isopropanol.[2] The exposure was performed by a scanning electron microscope (SEM) with a thermally assisted field-emission electron source using a commercial beam and stage control system.

The relationship between the electron energy and the required electron dose was determined by exposing patterns consisting of large and small scale structures. The required dose for small patterns (of the order of 10 nm) can be much larger than for large structures. In order to investigate this difference, the test patterns consisted of large areas connected to small lines with widths varying between 3 and 21 nm (as will be shown in detail later). These lines were written with a meander scan and a pixel separation of 3 nm. This structure also enables us to investigate proximity effects occurring at higher electron energies. The electron dose for the

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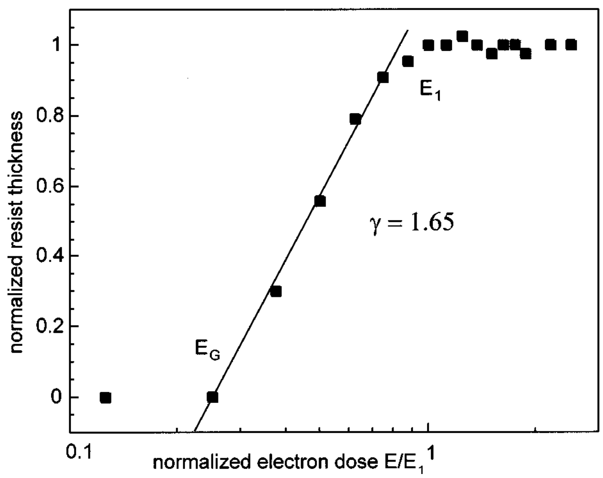

FIG. 1. Resist contrast curve for exposure at an electron energy of 2 keV. The minimum gel dose is $E_G = 200\ \mu C/cm^2$, and the saturation or maximum dose is $E_1 = 800\ \mu C/cm^2$. The contrast is measured to be $\gamma = 1.65$.

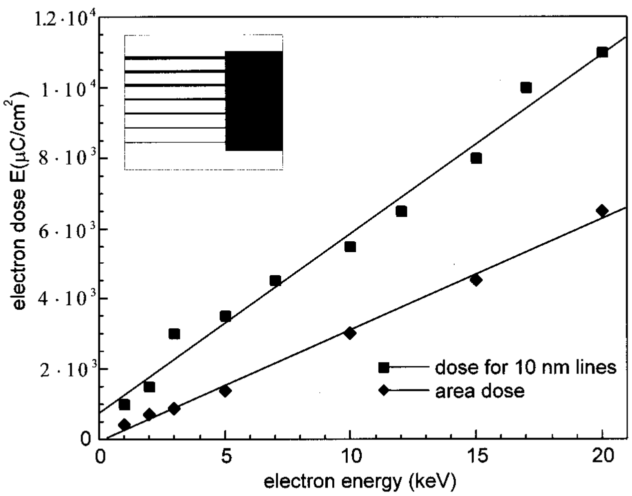

FIG. 2. Electron dose for 9–20 nm lines and for large scale patterns. The saturation dose for the large patterns was determined by measuring the resist thickness with an AFM, whereas the electron dose for the small features was controlled with a SEM. The inset shows the test structure used, where lines with different widths are connected to a large area with a lateral extension of $5 \times 20\ \mu m$. The nominal linewidth of the thinnest line is 3 nm (1 pixel line) and increases to 21 nm (7 pixels) for the thickest one.

small lines was determined by measuring the exposed linewidths in the developed resist with the SEM. The 100% dose was determined by requiring that the exposed linewidth be identical to the intended linewidth.

In the case of large patterns we determined the saturation dose required for a given resist thickness after exposure. For lower electron doses only a fraction of the resist film remained on the substrate after development.[7] This was confirmed by studies performed with an atomic force microscope (AFM) operating in the so-called tapping mode. The step height at the edges of the pattern as well as the slope of the film edge were also determined.

B. Irradiation damage

In order to investigate the influence of the electron beam at different energies on the quality of the underlying semiconductor layers, various Hall bar geometries were defined on a high-mobility GaAs/$Al_xGa_{1-x}As$ heterostructure grown by molecular beam epitaxy, where the two-dimensional electron gas is located 85 nm from the top surface. The Hall bar structures were defined using standard optical lithography and a wet chemical etching process. On the defined Hall bar structures a 42 nm thick calixarene film was subsequently exposed with different electron energies varying between 1 and 20 keV. The resulting electron density and electron mobility at 4.2 K were extracted from the period of the Shubnikov–de Haas oscillations in high magnetic fields and the resistance at zero magnetic field, respectively.[8]

III. RESULTS AND DISCUSSION

A. Exposure parameters

Figure 1 shows the resist contrast curve for an electron energy of 2 keV. The minimum gel dose is $E_G = 200\ \mu C/cm^2$, the saturation or maximum dose is $E_1 = 800\ \mu C/cm^2$. The contrast γ is defined as the slope of the line from E_G to E_1 and turns out to be $\gamma = 1.65$, in agreement with the value obtained previously for the exposure of calixarene films with 25 keV electrons.[7] Determining the maximum dose E_1, where the resist film achieves its maximum thickness, leads to the dependence of this saturation dose on the electron energy as shown in Fig. 2. Also shown in Fig. 2 is the required electron dose for the narrow lines. The inset in Fig. 2 shows an overview of the test structure used. Clearly, the electron dose for small structures exceeds the one for the large patterns by a factor of about 1.7 over the whole energy range considered.

Both plots in Fig. 2 indicate an almost linear relationship between the electron energy and the electron dose as predicted by Eq. (1) when the penetration depth of the incident electrons is much larger than the resist thickness.

The slope of the resist edge for different electron doses at an electron energy of 2 keV is shown in Fig. 3. For a dose of $500\ \mu C/cm^2$, just below the saturation dose, the maximum

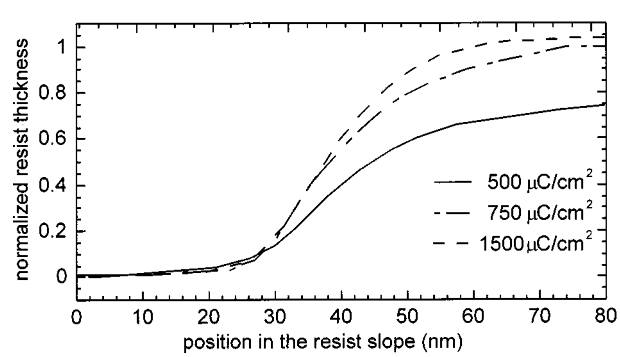

FIG. 3. Resist slope for electron doses of 500, 750, and 1500 $\mu C/cm^2$. Although the maximum resist thickness is almost achieved at $E = 750\ \mu C/cm^2$, the slope still gets steeper for higher electron doses.

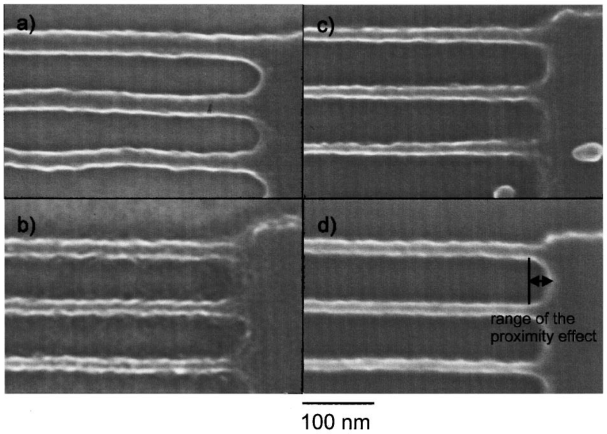

FIG. 4. (a)–(d) SEM picture of the test structure used for electron energies of 1, 2, 7, and 20 keV, respectively. Only a small influence of proximity effects can be seen at an electron energy of 20 keV, where the spatial range of the proximity induced line broadening is about 40 nm. At 1 keV (a) weak adhesion leads to curved lines.

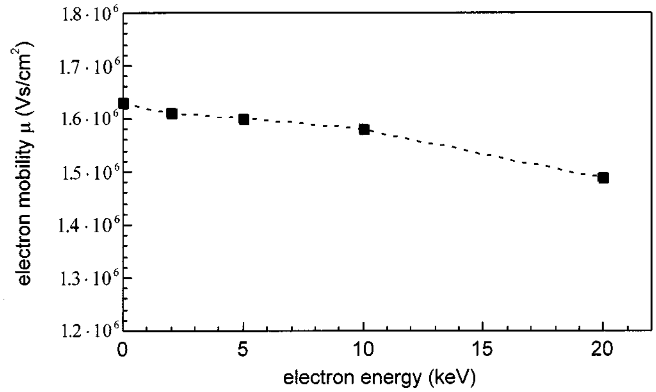

FIG. 5. Electron mobility in a high-mobility two-dimensional electron system after exposure of a 42-nm-thick calixarene film at different energies. The electron dose was chosen according to the saturation dose depicted in Fig. 2.

resist thickness is not yet achieved. Increasing the electron dose above the saturation dose of 800 μC/cm^2 to the dose required for the small lines of 1500 μC/cm^2 leads to a steeper resist slope. The width of the resist slope at the saturation dose allows one to estimate the range in which electron scattering is important to be about 40 nm. As has been found previously the scattering range is expected to follow a power law as a function of the incident beam energy:

$$\beta[\mathrm{nm}] = c \cdot W[\mathrm{keV}]^{1.7}, \qquad (2)$$

where c is of the order of 10.[9] For an incident beam energy of 2 keV the measured scattering range in our experiments is comparable to the value expected.

One advantage of low-energy electron-beam lithography is the reduction of proximity effects due to the reduced scattering range of the incident electrons. In addition, the range for direct electrodynamic interaction of the incident electron beam with the resist is smaller for lower electron energies.[10] In order to investigate the influence of proximity effects in calixarene, we determined the width of the thin lines in the vicinity of the large patterns in our test structure and found only small broadening due to proximity effects even at the highest electron energy of 20 keV (Fig. 4). The broadening turns out to be about 40 nm for all electron energies considered. We therefore conclude that proximity effects only play a role within a range of about 40 nm in the low-energy regime of electron-beam lithography with calixarene and are mainly caused by electrons scattered in the resist film, which has a thickness comparable to the observed scattering range. Backscattered electrons from the substrate could, in principle, lead to additional background exposure in the vicinity of the large patterns, especially for high beam energies. However, we do not observe any significant variation in the broadening for the beam energies considered and presumably this background exposure is smaller than the minimum gel dose E_G, making calixarene relatively insensitive to such proximity effects.

In our investigations we found a resolution limit of 10 nm for the lines used in our test structure even at accelerating voltages as low as 2 kV. Moreover, by connecting short lines at both ends, even at an electron energy of 2 keV, minimum structure sizes down to 6 nm were realized, suggesting that adhesion problems are responsible for the resolution limit. This is in good agreement with recent data of Fujita *et al.*, who found no change in resolution of a calixarene resist down to an electron energy of 5 keV, where the smallest possible structure size is about 10 nm. From Monte Carlo simulations they also concluded that the resolution limit of calixarene does not depend on the electron scattering but on weak adhesion to the substrate for structures smaller than 10 nm.[11]

Lowering the electron energy below 1 keV leads to reduced adhesion of the developed resist [Fig. 4(a)]. Calculations and measurements for a PMMA electron resist of 50 nm thickness indicate that below an electron energy of 1 keV the resist cannot be penetrated completely by the incident electrons.[5] In the case of positive resists this leads to a thin resist layer remaining after development, the thickness of which can easily be measured. For calixarene the whole thickness of about 42 nm was maintained even for an electron energy below 1 keV. Nevertheless, an unexposed thin film between the substrate and the exposed upper part of the resist layer leads to the observed reduced adhesion. A further reduction of the electron energy down to 500 eV results in the removal of the exposed film surface during the development process by dissolving the unexposed resist.

The dose reduction in low-energy electron-beam lithography can cause serious problems for electron resists with high sensitivity like PMMA due to shot noise in the electron beam. Since the shot noise limit is around a minimum number of about 200 electrons the limiting dose is about 150 μC/cm^2 for a resolution of 10 nm.[12] For calixarene, where the electron dose is 800 μC/cm^2 at an energy of 2 keV, the influence of shot noise is presumably already visible [Fig. 4(b)]. Thus, in addition to adhesion problems, shot noise turns out to be another limiting factor for high-resolution lithography at very low energies with calixarene.

B. Irradiation damage

We have measured the variation of the electron mobility in a high-mobility two-dimensional electron gas ($\mu = 166\,\mathrm{m}^2/\mathrm{V\,s}$) upon the electron energy in the lithographic process (Fig. 5).

A slight decrease of the electron mobility with increasing acceleration voltage is observed. Nevertheless, this effect plays only a small role in the energy regime considered. Since the total process of irradiation damage in electron-beam lithography is not yet fully understood, this result will be a topic of further research.

IV. SUMMARY

We have investigated the use of low-energy electron-beam lithography for the negative electron resist calixarene. The resolution limit at energies as low as 2 keV is found to be about 10 nm. The range of electron scattering in the resist film that leads to proximity effects was determined to be about 40 nm. Irradiation damage to a high-mobility two-dimensional electron gas in the low-energy regime evidently plays no significant role. Lowering the exposure energy of the electrons below 1 keV leads to incomplete vertical exposure of the resist film. We conclude that the most suitable energy regime for high-resolution low-energy electron-beam lithography with calixarene is in the range between 2 and 10 keV.

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