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Ellipsometric measurements of poly(methyl metacrylate) layers bembarded with boron ions*

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Poly(methyl metacrylate) (PMMA) is used as a material for masking layers in the process of the ion litography. Ellipsometric measurements have been used to establish the best technological conditions for achieving PMMA layers with the proper masking ability. The measurements of ellipsometric angles Δ and ψ allowed us to calculate the thickness (d) and the refractive index (n) of metacrylate-type layers in different spinning-on conditions, implanted with boron ions with energies 30 and 50 keV.

1. Introduction

The poly(methyl metacrylate), like many other organic materials dielectrics (SiO_2, Si_3N_4) and metals (Al), is used in form of thin layers as a masking stuff for controlled and selective technological processes.

The layer thickness depends on the effective range (projected range) of the implanted ions. This range is estimated by some electrical methods (e.g., the C-V technique) and non-electrical methods. The latter techniques are numerous and include among others the Auger electron spectroscopy (AES), the backscattered ion spectroscopy (RBS) and secondary ion mass spectroscopy (SIMS). Their sensitivity is, however, low when applied to polymer layers. Since, moreover, the layers undergo modification during the measurement, the applicability of the methods mentioned above is limited, and new methods for experimental works on the range of particles in polymers are required.

Ion litography technique [1, 2] was mentioned lately [3] as being useful in ion range measurements. The polymer chains degradation during the ion bombardment, and hence its solubility increase was applied.

The layer thickness after the development of polymer was used as the indicator of changes of its structure.

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In a case of relatively thick layers all ions are stopped in the layer, which is the only region where the changes caused by the ions are observable. But there exists also another case, when the layer thickness is smaller than the ion range and they are able to introduce changes in the substrate. Then, additional measurements of the substrate after the implantation should be performed.

The layer thickness was measured with the ellipsometric method. No need of any special preparation of samples before the measurement is its advantage.

Changes of the refractive index n of layers and substrates n_1 and the absorption coefficient k_1 of the silicon substrates can be measured as a function of the ion dose.

The ellipsometric measurements were done with EL–6 ellipsometer. Its characteristics were published before [4]. For the higher precision of the measurements of the refractive index and the layer thickness, they were performed at two wavelengths (550 and 600 nm) and two light incidence angles (65° and 70°). The experimentally found ellipsometric angles Δ and ψ were used for calculations of the values of n and d of the layer, when the parameters φ, λ, n_1 and k_1 are known, the last two values (n_1 and k_1) were measured ellipsometrically.

2. Experiment

Two kinds of the masking polymers (resists) have been tested. They have been produced in Research and Development Centre for Caoutchoucs and Vinyl Group-Plastics (Ośrodek Badawczo-Rozwojowy Kauczuków i Tworzyw Winylowych) at Oświęcim, Poland. The pure poly(methyl metacrylate) has been used as a standard material. Its technological parameters were described by other authors [5, 6]. The PMMA plastificated with di-butyl maleate has been chosed as the other material (PMMAm). Both the materials are described by the same parameters: $M_w = 230000$ and $M_w/M_n = 2$.

Solutions of the polymers were spin-coated on silicon substrates and next baked in the temperature of 443 K. The structures prepared in this way were bombarded with boron ions B^+ of the energies 30 and 50 keV.

The implanted resists were developed in the mixture of methyl-ethyl ketone and isopropyl alcohol 1 : 2 (vol). Implantation parameters have been chosen basing on theoretical works of other authors [7, 8]. According to ADESIDA [7], the projected range R_p of B^+ ions in PMMA is 1200 Å and 2900 Å for 30 and 50 keV, respectively. From the LSS theory and assuming [9], that the equivalent atomic number Z (PMMA) is 3.67, R_p can be estimated as 2670 Å, and standard deviation σ as 340 Å.

3. Results and conclusions

1. Implantation diminishes the thickness of the polymer layer (especially when the layers are thick) – Fig. 1. In the modified material the changes in the layer

thickness are smaller. This is a positive phenomenon for the reason of process stability.

2. Exposure characteristic slope (contrast) diminishes when the primary layer thickness increases. The modified poly(methyl metacrylate) has a better contrast. It is visible especially when the thick layers are considered (Fig. 2).

3. Some interesting properties of the modified resist (Fig. 3) are observed when analysing characteristics of the layer refractive index n. Implantation process causes an increase of the refractive index from 1.63 to 1.83 and then a decrease during the development. The same problem, but for the pure polymethyl metacrylate, was studied by WADA et al. [10]. They presented characteristics of the refractive index n as a function of ion dose and have found that its change from 1.48 to 1.80 is caused by amorphisation and carbonisation of the layer.

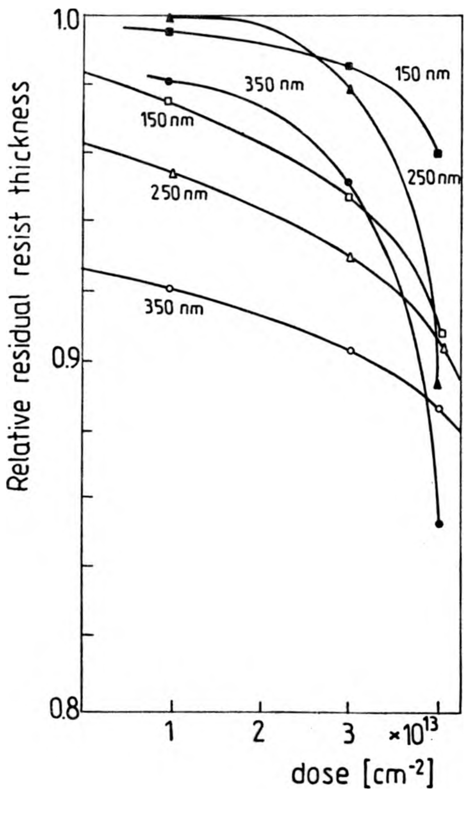

Fig. 1. Relative residual layer thickness (before development) of two different kinds of metacrylate-type polymers vs. B^+ dose, $E = 30$ keV: open signs – PMMAm (modified polymer), closed signs – PMMA (pure polymer)

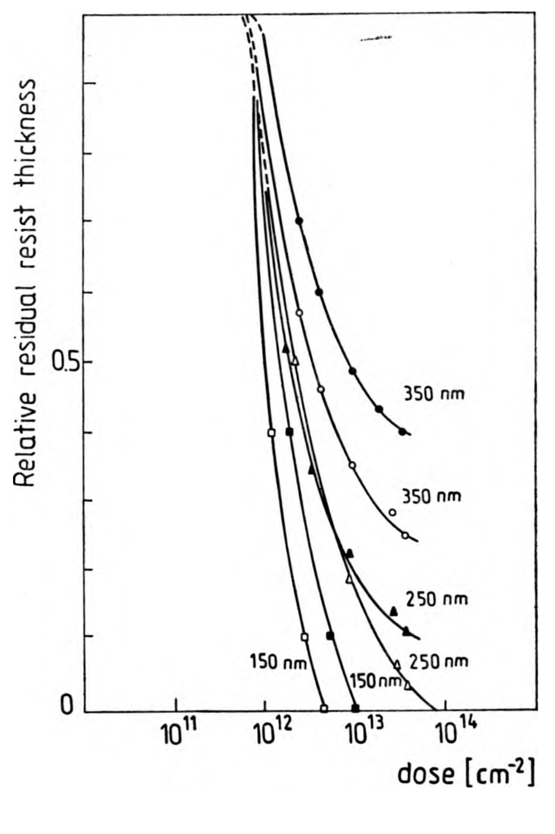

Fig. 2. Relative residual resist layer thickness of the developed polymers vs. B^+ dose, $E = 30$ keV, $M_w = 230000$ (for marking notation see Fig. 1)

The modified polymer is soluble in organic solvents (developers) after the implantation, i.e., no irreversible processes are caused by the bombarding ions.

4. B^+ ions implanted into Si change the optical parameters of the target (Fig. 4). They are observable starting with the dose of 10^{13} cm^{-2}.

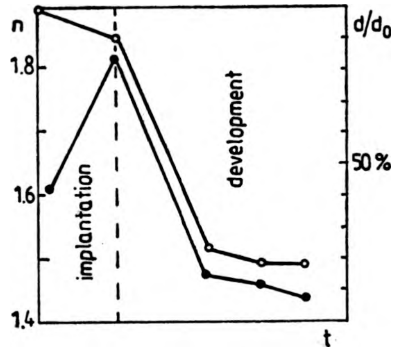

Fig. 3. Refractive index n (○) and relative resist thickness d/d_0 (●) vs. time (arbitrary units) during the processes of implantation and development

5. Figure 5 shows the theoretical ellipsometric curve (open circles) with experimentally obtained points (closed circles) for different ion doses. Good accordance of the theory and the experiment is visible.

The ellipsometric method proved to be a useful tool for ion range measurements. Its application to ion litography enables the control of technological processes without destruction of samples and preserving the optimization parameters.

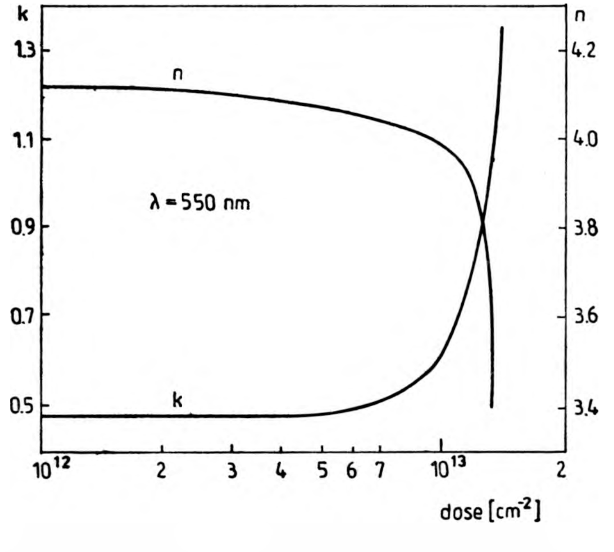

Fig. 4. Absorption coefficient k and refractive index n of Si vs. B^+ dose

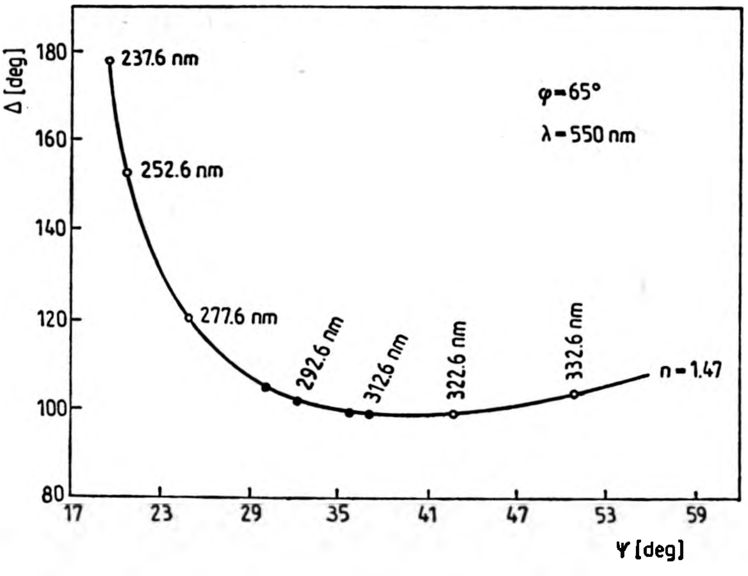

Fig. 5. Theoretical ellipsometric curve (○) with experimentally obtained points (●) for different ion doses

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Эллипсометрические исследования слоев полиметакрилата метила (PMMA), бомбардируемых ионами бора

Полиметакрилат метила применяют в качестве маскировочного слоя. Для определения режима накладывания слоев PMMA, хорощо маскирующих основание, применяют эллипсометрические исследования. На основе измерений углов Δ, ψ определены толщины (d) и коэффициенты преломления (n) слоев полиметакрилата метила, нанощенного в разных режимах, боибардированного ионами бора с энергией 30 и 50 кэв.