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The synthesis of silicon nitride layers in a planar induction reactor

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Abstract

A method is developed for the synthesis of silicon nitride layers using planar inductive activation of reagent gases: monosilane and nitrogen (or ammonia). Mechanical characteristics of the resulting silicon nitride films were investigated with the help of ellipsometry. The composition of the synthesized layers was studied by means of IR spectroscopy. It is shown that the amount of hydrogen and the nature of its bonding in the growing silicon nitride layers are determined by synthesis temperature and nitrogen or ammonia to monosilane ratio [N_2/SiH_4] in reagent flow. A decrease in the total hydrogen content of films to 4% was observed with [N_2/SiH_4]=3. Under this technological mode of synthesis, an increase in the concentration of Si–N bonds occurs along with a decrease in the concentrations of Si–H and N–H bonds. The developed synthesis method allowed us to synthesize silicon nitride layers with low hydrogen content (4%) from nitrogen and monosilane at a temperature below 300 °C. Technological regimes were determined for the route of manufacture of the microbolometric matrix.

Keywords: Ellipsometry; Adsorption porometry; Fourier transform infrared spectroscopy; Plasma chemical silicon nitride

1. Introduction

At present, growing attention is attracted to micromechanical structures, in particular, to bridge-structured microbolometers made of plasma chemical silicon nitride, which are winning the leading positions in the world market of thermal imagers [1]. Silicon nitride for these purposes is usually synthesized in *hf*-capacitance reactors. The disadvantages of this type of reactors are: complicacy of obtaining homogeneous plasma with low ion energy on a large area, and high hydrogen content (20%) in the obtained films, even if the process is conducted at a temperature of 400 °C. Hydrogen is assumed to be the reason of instability of the physicochemical properties of microconstructions of silicon nitride. The authors of [2] who used the induction reactor of Plasma-Therm demonstrated the possibility to decrease mechanical strain in silicon nitride by adjusting the parameters of ion beam bombarding the growing film. The authors of Ref. [3] showed that variations in the distribution of bound hydrogen between different chemical bonds in silicon nitride depend on synthesis conditions.

The plasma chemical setup with the planar induction reactor of the new generation, developed by us, allows performing technological processes with ion beam densities at a level of 10^{11} cm^{-3} and with low ion energy, as a rule below 100 eV. This reactor provides the possibility to obtain dielectric layers which are uniform in thickness and contain minimal amount of defects on substrates with a diameter more than 150 mm. Using this setup, we chose optimal parameters and developed the processes for the synthesis of silicon nitride layers using monosilane, ammonia and nitrogen as initial reagents. Developing an approach described in Ref. [3], we realized the possibility to obtain layers with low mechanical strain and low content of bound hydrogen in the silicon nitride layers synthesized from monosilane and ammonia with the addition of small amount of oxygen. To optimize the synthesis processes and to investigate mechanical characteristics of the synthesized films, we used a new nondestructive procedure involving ellipsometry. We investigated physicochemical and electro-

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physical properties of the synthesized layers and determined technological modes for the route of manufacture of microbolometric matrix.

2. Experimental

The synthesis of silicon nitride and oxynitride layers was performed in a plasma chemical setup. The setup includes a planar induction reactor of the new generation allowing one to conduct the synthesis of dielectric layers using the ion beam density at a level of 10^{11} cm^{-3} and above, and low ion energy, as a rule below 100 eV. A scheme of the planar induction reactor is shown in Fig. 1. The use of spiral inductor in the reactor provides the possibility to obtain uniform plasma over a large area up to 300 mm in diameter. The design of the reactor provides the admission of nitrogen or ammonia into the region with maximal plasma density (skin layer), which in the case under consideration is ion source of large area and density, while silane is admitted into the region behind the skin layer. The use of an additional high-frequency shift on the substrate allows governing the energy of ions that bombard the surface, independently of the density of ion beam assigned by the induction source.

The working frequency of the generator was 13.56 MHz and the power was not more than 1 W/cm^2. Initial reagents were nitrogen or ammonia, a 5% mixture of monosilane with argon, and oxygen (99.999%). The ratio (R) of ammonia (nitrogen) to silane concentration in the flow was varied from 3 to 20, at the constant oxygen concentration in the flow. Changes in the reagents ratio R and/or temperature caused variations in the distribution of hydrogen chemically bound in silicon nitride, as well as changes in the film structure and mechanical strain in the film. The working pressure in the reactor was (5 to 6)$\times 10^{-2}$ Torr.

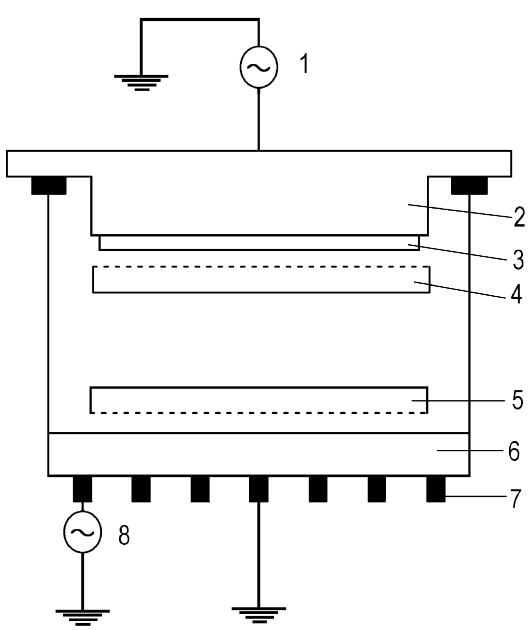

Fig. 1. A scheme of the reactor: 1, shifting potential; 2, substrate heater; 3, sample; 4, admission of silane and oxygen; 5, admission of ammonia or nitrogen; 6, quartz window; 7, spiral inductor electrode; 8, HF generator.

All the films were grown on (001) silicon substrates. They were of approximately equal thickness (100 to 110 nm), and synthesis temperature was varied from 20 to 300 °C.

Ellipsometric measurements were performed with a high-vacuum ellipsometric setup. A fast-operating automatic LEF-701 ellipsometer has the working wavelength of λ=632.8 nm; angle of light incidence on the sample was ϕ_o=70°. The multiangle measurements (5 angles) were performed with a hand-operated LEF-3A ellipsometer.

Transmission spectra of the films were recorded with Bruker IFS-113V Fourier Transform spectrometer within 400 and 4000 cm^{-1}, with a resolution of 1 cm^{-1}.

3. Results and discussion

The silicon nitride layers (obtained with the initial reagents: SiH_4 (5%) in argon+NH_3+O_2) were characterized by thickness scattering less than 1% and low mechanical strain. The plasma chemical silicon nitride synthesized at a temperature of 300 °C contains hydrogen at a level below 4%, which corresponds to silicon nitride obtained at temperatures above 800 °C by means of chemical vapor deposition.

3.1. Adsorption curves

The investigation of films by means of adsorption porometry using ellipsometry indicated that the films have porous structure; their porosity is not more than 10%. Toluene was used as adsorbate. The method was described in detail in Refs. [4,5]. Porosity depends on synthesis conditions. Mean pore radius is about 3.5 nm. The distribution of pores for different temperature points (25, 100 and 220 °C) with R=3 is shown in Fig. 2.

To examine the rigidity of the framework of resulting layers, we applied the adsorption ellipsometric procedure. Capillary forces, which arise in pores during adsorption, depend mainly on pore size. If the mean pore radius and concentration are known, we may estimate pressure occurring in the pores and detect a level above which the film structure gets destroyed. If other conditions are kept constant and pore size does not vary much, the behaviour of the film during adsorption will depend on the rigidity of the film framework. The main factor affecting the structure (porosity) of the resulting films is the process temperature. The films obtained at a temperature of 20–45 °C have very friable structure; adsorption proceeds irreversibly on these layers; capillary forces destroy the film framework during adsorption. Uniform compression of the film during adsorption is characteristic of the layers obtained at 20 °C, while for the