ISSN 1063-7826, Semiconductors, 2016, Vol. 50, No. 2, pp. 167–170. © Pleiades Publishing, Ltd., 2016.
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SURFACES, INTERFACES, AND THIN FILMS

Study of the Surface of GaAs after Etching in High-Frequency and Glow Discharge Plasma by Atomic Force Microscopy

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Submitted April 21, 2015; accepted for publication April 30, 2015

Abstract—The quality of the surface of a semiconductor structure after plasma-chemical etching in plasma of HCl/Ar, HCl/Cl_2, HCl/H_2 mixtures, and freon R12 plasma is studied. It is shown that the optimal combination of the etch rate and surface roughness is achieved in the hydrogen chloride and argon mixture. In mixtures with hydrogen, the etch rates are too low for high surface quality; in mixtures with chlorine, the surface roughness exceeds technologically acceptable values due to high etch rates. The high-frequency discharge in freon R12 can be effectively used to etch semiconductors, providing technologically acceptable interaction rates, while retaining a uniform and clean surface.

DOI: 10.1134/S106378261602007X

1. INTRODUCTION

It is clear that the technological process of producing modern electronics requires dimensional structuring of the substrate surface to achieve a tailored high-resolution topological relief. This problem can be solved only by plasma etching methods. Chlorine-containing gas plasma is used in electronics technology for the cleaning and dry etching of semiconductor wafers and functional layers of integrated circuits. GaAs, which is a promising material of future electronics and is the basis of a wide range of high-frequency high-speed devices [1], was used as the sample to be studied.

Due to the high integrated density of modern electronic devices, requirements for surface quality after plasma treatment are very high. Currently, halogen-containing gases, in particular mixtures based on Cl_2 are used as plasma-forming media [2, 3]. The main disadvantage of chlorine plasma is the low anisotropy caused by its high activity, which leads to significant surface-relief enhancement after treatment. In practice, chlorine-containing gases only are rarely used as plasma-forming etching media. Commonly, plasma-forming etching media are multicomponent mixtures. In technology, mixtures of chlorine-containing gases, their mixtures with inert (He, Ar) and molecular (O_2, H_2) gases, and complex multiatomic gases such as freon R12 (CCl_2F_2) are widely used.

After all the aforementioned there still remains the problem regarding methods for controlling the surface of a semiconductor after etching. From the viewpoint of the relief study, one of the most promising methods is atomic-force microscopy (AFM) whose main advantages are the possibility of obtaining reliable data on the microrelief height, the absence of additional intermediate procedures reducing result reliability, the possibility of achieving nanoscale resolution in air, and others.

In previous studies [4, 5], we comparatively studied the kinetics and mechanisms of the plasma-chemical etching of GaAs in Cl_2 and HCl at identical external parameters of the discharge. It was found that the behavior of etch-rate variations with the discharge current and gas pressure is consistent with variations in the chlorine-flow density on the treated surface in both systems. HCl plasma exhibits lower GaAs etch rates (e.g., three times larger in comparison with Cl_2 plasma at a pressure of $p = 80$ Pa and discharge current of $i_p = 40$ mA), but provides a much lower surface roughness after treatment. The latter can be explained by reactions of hydrogen atoms.

The objective of this work is to directly study the quality of the semiconductor-structure surface after plasma-chemical etching in the glow-discharge plasma of HCl/Ar and HCl/Cl_2 mixtures and in freon R12 plasma of high-frequency (HF) discharge.

2. EXPERIMENTAL

The plasma–GaAs interaction was experimentally studied under conditions of dc glow discharge using a cylindrical flow-through plasma-chemical reactor (inner diameter $d = 3.4$ cm and discharge-region length $l = 40$ cm). The discharge current ($i_p = 10$–60 mA) and pressure ($p = 100$ Pa) of the plasma-forming gas were used as external discharge parameters.

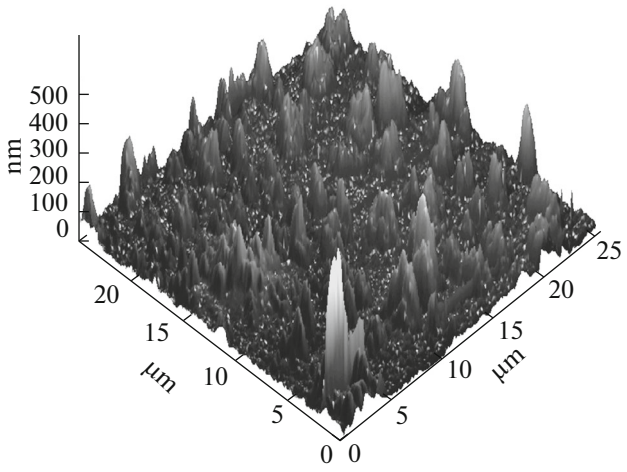

Fig. 1. GaAs surface etched in HCl/Ar plasma with a component ratio of 60/40, at $i_p = 40$ mA for 300 s; $\sigma \approx 40$ nm.

HCl was produced by a chemical method based on the reaction between sodium chloride and sulfuric acid [6]. Argon, hydrogen, and chlorine were used as a component of the gas mixture. Pure-grade argon was taken from gas cylinders (MRTU (inter-republican technical specifications) 51-77-66); the main gas content is no less than 99.985%. Hydrogen was produced by a method based on the chemical reaction between Zn and HCl; the reaction was performed using Kipp's apparatus [6]. Chlorine was produced by the thermal decomposition of chloric copper in vacuum [6]. The gas purity was preliminarily verified by discharge-emission spectra; the gas pressure was measured using a U-shaped oil manometer.

The plasma-chemical processes under HF discharge conditions were studied using a Platran-100KhT setup. It is intended for the plasma-chemical etching of semiconductor materials and metal films whose reactions with plasma-forming gas mixtures based on chlorine and fluorine form volatile compounds. The setup makes it possible to process a wafer of up to 100 mm in diameter and smaller with a thickness from 0.3 to 2 mm.

The system was evacuated using a Leybold BCS mechanical rotary vane pump (with an output of 30 m^3/h) and a TMP 803 LMTC turbomolecular pump (with an output of 800 L/s) to a limit residual gas pressure of ~10^{-6} Torr. The operating pressure in the reactor was verified by a capacitive sensor (baratron) with an upper measurement limit of 0.1 Torr. The plasma-forming gas flow rate was measured and controlled using flowmeters with an upper limit of 500 cm^3/min. The temperature control system provides automated stabilization of the substrate temperature by varying the cooling-liquid flow rate. In the present experiments, the power deposited to the discharge was constant, 950 W; the plasma-forming gas flow rate was 20 cm^3/min (~1.4 mTorr). The etching time was varied from 30 to 150 s with an interval of 30 s.

The samples subjected to etching represented fragments of polished GaAs wafers (400 μm thick). The sample surface relief was monitored using a Solver P47-PRO atomic-force microscope which allows study of the sample surface for areas of up to 50 × 50 μm in size.

3. RESULTS AND DISCUSSION

As noted above, one of the most important etching aspects in technology is the surface quality factor after etching. In [4, 7], it was noted that chlorohydrogen plasma allows the polishing etching of GaAs, providing high uniformity and high cleanness due to the efficient removal of oxides and impurities by atomic hydrogen. The surface GaAs treated in pure chlorine-containing gases, in particular in chlorine and chlorohydrogen, has been repeatedly presented as micrographs in our previous papers [7–9]. As for HCl plasma, it was argued that the sample surface remains relatively smooth even after maskless etching. The root-mean-square roughness in HCl plasma is $\sigma \approx$ 120 nm. For unetched gallium-arsenide samples, this parameter was ~10 nm on average. We note that the GaAs etch rates we observed in the glow discharge plasma for pure Cl_2 were above the upper limit of the technologically acceptable range which is 0.2–0.5 μm/min [7, 10]. At such rates, nonuniform etching of the samples, etch-product redeposition on the treated material, and other undesirable effects are possible.

The surface quality deteriorates as a result of etching and the root-mean-square surface roughness is $\sigma =$ 330 nm.

Micrographs of GaAs sample surfaces treated in a HCl/Ar mixture are shown in Fig. 1. The surface quality is visually higher than that for HCl plasma, and this is the case: the root-mean-square roughness is $\sigma \approx$ 40 nm. This might be expected, the spontaneous interaction rate is lower in the mixture; therefore, the resulting surface roughness should also be smaller. However, it should be noted that the root-mean-square roughnesses are close for HCl/Ar compositions with component ratios of 80/20, 60/40, and 40/60 at $i_p = 40$ mA, despite the significant difference in material treatment rates. This means that ion enhancement of the desorption is much more efficient under conditions of mixtures than for undiluted HCl plasma, and the effect of surface "micromasking" by interaction products is weaker. The above suggests that inert gases, in particular argon, can be merely dilute gases (a decrease in the concentration of active particles, an increase in the process anisotropy, and a decrease in plasma-forming gas consumption) and ion sources for additional ion enhancement of interaction product desorption.

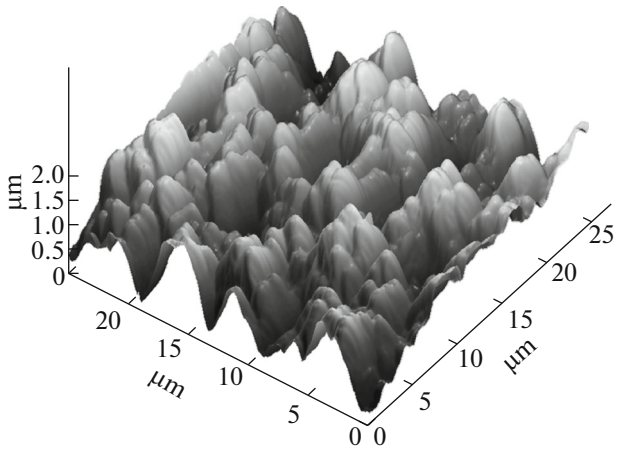

Fig. 2. GaAs surface etched in HCl/Cl_2 plasma with a component ratio of 60/40 at $i_p = 40$ mA for 300 s; $\sigma = 330$ nm.

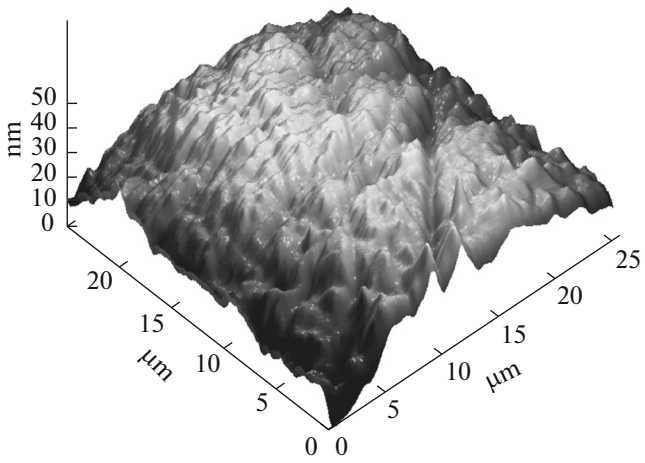

Fig. 3. GaAs surface etched in HCl/H_2 plasma with a component ratio of 60/40 at $i_p = 40$ mA for 300 s; $\sigma \approx 20$ nm.

Figures 2 and 3 show the GaAs sample surfaces treated in HCl/Cl_2 and HCl/H_2 mixtures. As for the HCl/Cl_2 mixture, it should be noted that etch rates are comparable to the rates in pure chlorine plasma [4, 10]; therefore, a result similar to that obtained for treatment in pure chlorine was expected. At a discharge current of $i_p = 40$ mA, the rate of the spontaneous chemical interaction increases almost three times. This results in an extremely rough surface typical of treatment in pure Cl_2 plasma, with obvious traces of structural damage and the redeposition of material and interaction products on the sample surface. The root-mean-square roughness is $\sigma = 330$ nm. This is by no means always acceptable in modern micro- and nanoelectronics technology.

For the samples etched in the HCl/H_2 mixture, at a component ratio of 80/20, σ directly correlates with changes in the treatment rate. In the case of further dilution (60/40), σ is already at a level close to σ of the unetched samples, the micrographs show the slight removal of a small material surface layer. Samples whose mass loss was not detected gravimetrically were also scanned; the obtained micrographs are almost identical to the micrographs of samples not subjected to plasma-chemical processing. Thus, hydrogen chemistry provides polishing etching while retaining the surface stoichiometry; however, the etch rates are very low and often unacceptable from the viewpoint of technology [11].

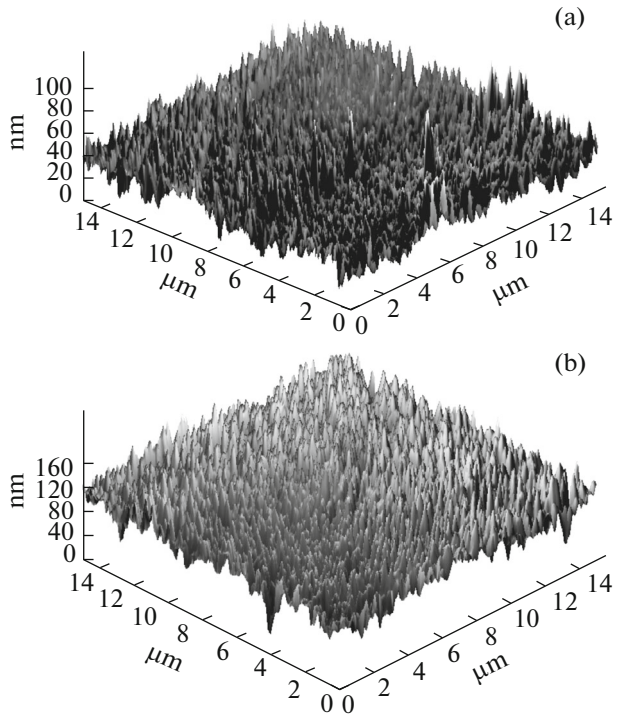

Fig. 4. GaAs surface etched in freon R12 plasma. The HF discharge power is 950 W and the pressure is 1.4 mTorr. The treatment time is (a) 90 s ($\sigma = 11$ nm) and (b) 150 s ($\sigma = 14$ nm).

Figures 4a and 4b show the micrographs of sample surfaces subjected to etching in freon R12 (CCl_2F_2), depending on the exposure time. We can see that the sample surface changes; this is also true for the roughness: σ changes from 7 to 14 nm at treatment times of 30–150 s. An increase in σ is predictable under conditions of increasing time of interaction of chemically active plasma particles with a semiconductor sample. Such a change in the surface quality is very characteristic of halogen-containing gases and is acceptable from the viewpoint of technology [2, 4]. An increase in the plasma–sample interaction time to 300 s consequently results in an almost threefold increase in the root-mean-square surface roughness of the semiconductor to ~45 nm. These results are comparable to the data obtained for HCl/Ar and HCl/H_2 mixtures under conditions of dc glow discharge, which allows us to

speak of freon R12 plasma as a very effective tool for etching GaAs while retaining a surface quality typical of chlorohydrogen chemistry.

4. CONCLUSIONS

The quality of a gallium-arsenide surface after etching in plasma of HCl/Ar, HCl/Cl_2, and HCl/H_2 mixtures was comparatively studied. The plasma of chlorohydrogen and its mixtures allows etching with better uniformity and cleanness. The effect of etching conditions and mixture compositions on the quality of the treated surfaces was studied. It was shown that the optimal combination of the etch rate and surface roughness is achieved in the mixture of hydrogen chloride with argon. In mixtures with hydrogen, the etch rates are too low for high surface quality; in mixtures with chlorine, the surface roughness exceeds technologically acceptable values due to high etch rates.

The high-frequency discharge initiated in a freon R12 gas medium can be efficiently used to etch semiconductors, in particular, gallium arsenide, providing technologically acceptable interaction rates, while retaining a uniform and clean surface.

Thus, freon R12 is a promising plasma-forming gas and can be used in microelectronics technology.

ACKNOWLEDGMENTS

This study was performed within a basic part of a State contract.

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Translated by A. Kazantsev