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ENHANCEMENT OF CF_4 AND O_2 REACTIVE ION ETCHING RESISTANCE OF POLY(BUTENE-1 SULFONE) BY N_2 PLASMA PRETREATMENT

Indexing terms: Plasmas, Photolithography, Semiconductor doping, Semiconductor growth

The resistance of poly(butene-1 sulfone) (PBS) to CF_4 and oxygen reactive ion etching is greatly enhanced by low power nitrogen plasma pretreatment. The original thickness of PBS can be maintained.

Introduction: Poly(olefin sulfones) are sensitive *e*-beam positive resists which are used primarily as wet-etch masks for the fabrication of chrome photomasks.[1] Poly(olefin sulfones) have found little use as dry-etch masks because of their lack of plasma etching resistance. Mansfield[2] reported the resistance enhancement of poly(butene-1 sulfone) (PBS) to fluorocarbon etching by oxygen plasma pretreatment (100 W, 0·5 Torr, 3 minutes, 16°C). However, resist thickness loss is observed in this oxygen plasma pretreatment. PBS itself is insensitive to mid or deep UV light exposure. We found that the exposure sensitivity of PBS can be greatly increased by the addition of a catalytic amount of deep UV sensitive photoacid.[3] Thus, PBS can be used as a deep UV positive-tone resist. We report that PBS's resistance to CF_4 and oxygen reactive ion etching (RIE) can be much enhanced by nitrogen plasma pretreatment with power lower than 80 W. The original thickness of PBS can be maintained.

Experimental: PBS with an average molecular weight of 660000 was obtained from Polysciences Inc. The PBS was dissolved in methylethylketone (MEK) and spincoated on silicon wafers for this study. RIE was performed with a Vacutec plasmatch system. FT-IR spectra were recorded with a Nicolet 520 FT-IR spectrometer. The glass transition temperature of PBS was determined by using a Seikoi SSC-5200 differential scanning calorimeter. Auger electron spectra were taken using a VG Microlab Mark-III. ESCA was recorded with a Perkin Elmer ϕ-548. PBS film thickness was read from a Rudolph EL-III ellipsometer and a Dektak IIA surface profilometer.

Results and discussion: The remaining film thicknesses of PBS before and after CF_4 and O_2 RIE as a function of N_2 plasma treatment power are shown in Fig. 1. The plasma treatment and RIE conditions of Fig. 1 are as follows:

	N_2 plasma	CF_4 RIE	O_2 RIE
Power (W)	20, 30, 50, 80	30	25
Pressure (mTorr)	500	100	30
Flow rate (sccm)	50	20	20
Treatment/etch time (minutes)	5	1	1
DC bias (− V)	~20, 30, 50, 80	~30	~25

The results indicate that the intial thickness of PBS was maintained by N_2 plasma treatment under the conditions used and resistance to CF_4 RIE is much enhanced. The resistance of PBS to O_2 RIE is also enhanced considerably, but is a factor

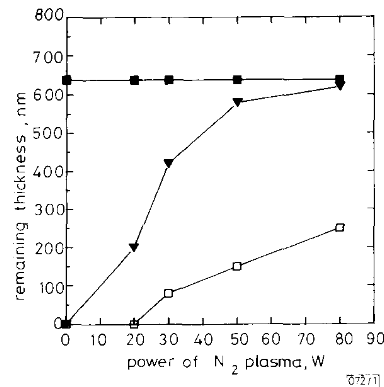

Fig. 1 *Remaining thickness of PBS by N_2 plasma treatment only, by N_2 plasma treatment followed by CF_4 RIE and followed by O_2 RIE, as functions of power of N_2 plasma*

PBS original thickness = 638 nm
■ N_2 plasma treatment
▲ CF_4 RIE
□ O_2 RIE

of two or three less resistant than observed with CF_4 RIE. The PBS is not an Si-containing polymer, thus its resistance to O_2 RIE has limitations.

The RIE resistance of PBS is dependent on the N_2 plasma and RIE variables. We found that the power of N_2 plasma treatment is a dominant factor. The thickness of PBS cannot be maintained if the power of the N_2 plasma is higher than 80 W. FT-IR spectra of untreated and N_2 plasma treated PBS are shown in Fig. 2. The formation of several new absorption peaks after N_2 plasma treatment are found and marked A ($3300\,cm^{-1}$), B ($1700\,cm^{-1}$), and C ($1600\,cm^{-1}$) and are

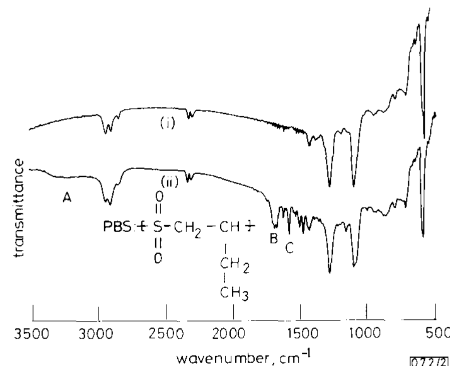

Fig. 2 *FT-IR spectra of untreated and N_2 plasma treated PBS*

Chemical formula of PBS is also shown
N_2 plasma conditions are as follows: flow rate = 50 sccm, pressure = 500 mtorr, power = 30 W, time = 5 minutes
(i) Untreated PBS
(ii) N_2 plasma treated PBS

assigned as stretchings of N—H, C=O and C=C, respectively. The decrease by about one quarter absorption of other two peaks at 1300 and $1130\,cm^{-1}$ which are the symmetric and asymmetric S=O stretchings is also found. The source of oxygen of C=O bond is probably from the S=O sidechain scission and/or due to the presence of oxygen impurity.[4]

The Auger electron spectra of carbon (KLL) of PBS as shown in Fig. 3 illustrate a 2·4 eV kinetic energy shift from 273·9 to 276·3 eV as a result of the N_2 plasma treatment. This kinetic energy shift is interpreted as indicating that the carbon atom becomes more electropositive because of the formation

of many C=O and C=C bonds as indicated in the FT-IR spectrum. Because the existence of N—H bonds is found in

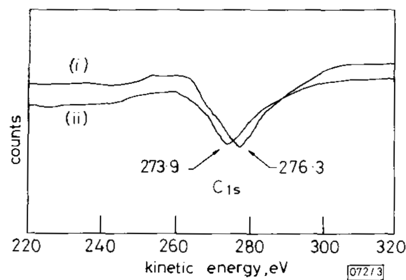

Fig. 3 *Carbon (KLL) Auger electron spectra of untreated and N_2 plasma treated PBS*

N_2 plasma conditions are same as Fig. 2
(i) N_2 plasma treated PBS
(ii) Untreated PBS

the FT-IR spectrum, there is also the formation of C—N bonds. Therefore, a core electron of carbon is shifted to a higher binding energy due to the carbon atom becoming more electropositive. Consequently, a corresponding chemical shift in the Auger electron kinetic energy is observed.

The ESCA analysis also indicates the existence of a significant amount of nitrogen with a binding energy of 398·9 eV in the N_2 plasma treated PBS. It would therefore appear that a nitrogen atom is clearly involved in the new bond formation of the hardened chemical composition of PBS. The glass transition temperature (T_g) of PBS is increased by about 10°C as shown in Fig. 4 and indicates that a certain degree of crosslinking occurs in PBS after N_2 plasma treatment.

The reduction of positive or negative resist flow during postbake as a result of N_2 plasma pretreatment has been

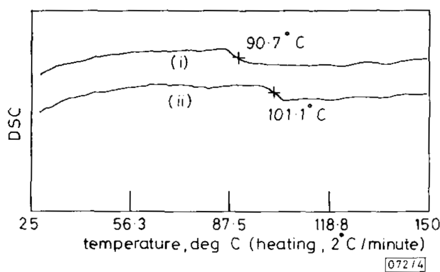

Fig. 4 *Differential scanning calorimetry (DSC) measurements showing glass transition temperature (T_g) of untreated and N_2 plasma treated PBS*

N_2 plasma conditions are same as Fig. 2
(i) Untreated PBS
(ii) N_2 plasma treated PBS

reported.[5] The creation of a hardened shell at the surface is suggested. In our study, although the natures of the chemical reactions responsible for these enhanced RIE resistances after N_2 plasma treatment are not fully known, it is believed that the crosslinking of PBS molecular chains is the most important cause. Depolymerisation of PBS is inhibited or retarded. Surface modification of PBS by the formation of some RIE resistant functional groups is also postulated.

Conclusions: Enhancement of CF_4 and N_2 RIE resistance of PBS by N_2 plasma pretreatment has been demonstrated. The original thickness of PBS can be maintained. Further study is needed to clarify the chemical composition and mechanisms involved.

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SELFSTARTING, PASSIVELY MODELOCKED ERBIUM FIBRE RING LASER BASED ON THE AMPLIFYING SAGNAC SWITCH

Indexing terms: Lasers, Optical fibres, Nonlinear optics

A novel self-starting, passively mode-locked erbium fibre laser is reported. The scheme is based on the reflection properties of a nonlinear amplifying loop mirror and provides a stable source of picosecond pulses.

Nonlinear optical loop mirrors (NOLMS)[1] are of considerable interest for optical switching and modelocking of fibre lasers. Reverse biased NOLMS[2] have already been incorporated in conventional active modelocking systems to act as intracavity pulse compressors* and also as all-fibre passive modelockers.[3] However, in such systems the requirement for loop biasing by means of induced fibre birefringence leads to polarisation control problems and hence to environmental instability. Recently, nonlinear amplifying loop mirrors (NALMS)[4,5] have been shown to offer improved pulse switching properties both in terms of input switching power (full amplitude switching powers as low as 200 μW have been reported)[4] and on/off contrast. We report on the use of a unbiased NALM in an all-fibre, self-starting, passive modelocking configuration. We believe this development will lead to remarkably simple, stable and practical sources of picosecond pulses at 1·55 μm for soliton communication systems.

The laser configuration is shown in Fig. 1. At low input powers the NALM acts as a conventional loop-mirror reflecting light back to the port from which it came. Thus low intensity light circulating anticlockwise in the isolator loop

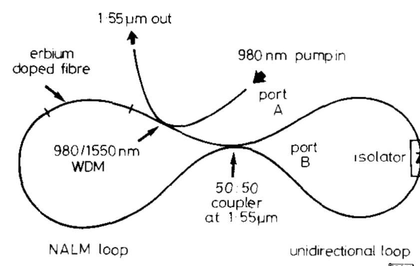

Fig. 1 *Experimental configuration of selfstarting, passively modelocked fibre laser*

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