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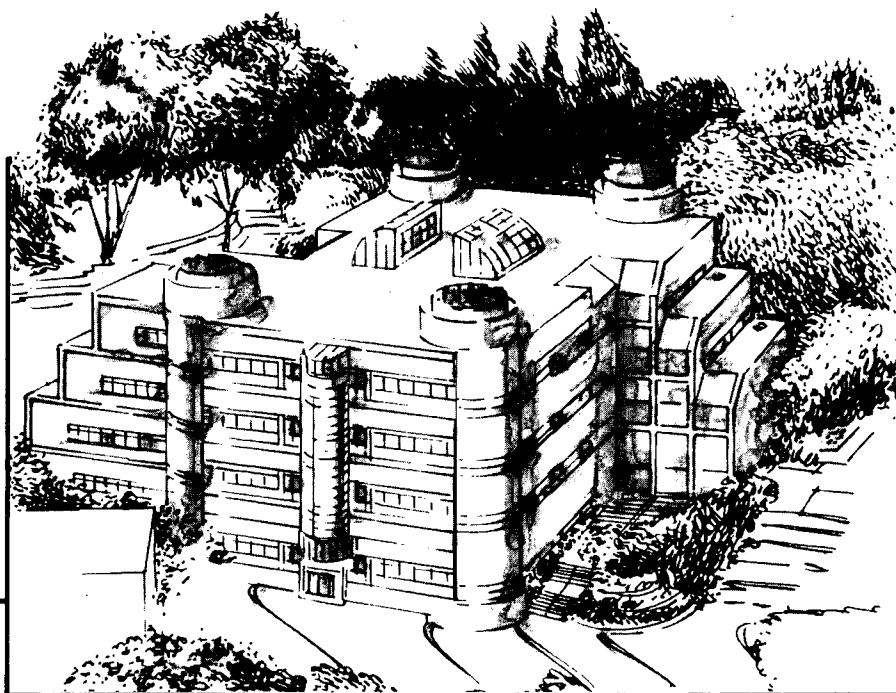
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OBSERVATION OF CRYSTALLINE C₃N₄

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OBSERVATION OF CRYSTALLINE C_3N_4

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ABSTRACT

We present strong experimental evidence suggesting that we have synthesized the β - C_3N_4 phase. This is a new material predicted by theory to have bulk moduli comparable to diamond. Thin films containing small crystals were deposited on Si and Ge wafers by RF diode sputtering of a pure graphite target with pure N_2 . The crystal structure of these phases was investigated using X-ray and electron beam diffractometry as well as transmission electron microscopy. Our results indicate that the β - C_3N_4 particles with typical dimensions of $\sim 0.5\mu m$ and are embedded in a $1\mu m$ thick layer of a C-N polymer. These particles are believed to crystallize preferentially on Si (100) wafers.

Recently Liu and Cohen¹ reported a theoretical calculation which suggests that covalent C-N solids could have bulk moduli comparable to diamond and hence are good candidates for new hard materials. The calculation was motivated by an empirical model² for the bulk moduli of tetrahedral solids which indicates that short, low ionicity bonds, such as those which form between C and N, are favorable for achieving a high bulk modulus. Using the simpler of the two known Si₃N₄ crystal structures as a prototype, Liu and Cohen performed a first principles pseudopotential total energy calculation to investigate the structural and electronic properties of β -C₃N₄ (C₃N₄ in the β -Si₃N₄ structure). The bulk modulus of the hypothetical compound β -C₃N₄ was found to be comparable to that of diamond. In addition the cohesive energy of β -C₃N₄ was calculated to be moderately large, indicating that it could be a metastable structure. These results suggest that the synthesis of a new hard C-N solid, which could have technological applications, may be possible.

The deposition of amorphous carbon nitride thin films have been attempted by Jones and Steward³ using plasma decomposition of nitrogen and various hydrocarbons, and by Han and Feldman⁴ using rf plasma deposition. Nitrogen contents ranging from 0-40% in the amorphous films were achieved by these authors. However, identification of a crystalline carbon nitride material has not been reported. In 1990 we have documented the synthesis of crystalline C₃N₄ material using the sputtering technique⁵. Since then there have been several reports on the positive identification of C₃N₄ crystals in the literature⁶⁻⁹. In this letter we report on our attempt to synthesize the predicted β -C₃N₄ phase by means of thin film deposition techniques. The experimental results support the presence of the crystalline β phase on (100) oriented Si substrates.

The experimental approach involved the production of thin films containing carbon and nitrogen (C-N films) deposited on oriented single crystal Si and Ge wafers by means of the RF diode sputtering technique at a frequency of 13.56 MHz. The target consisted of an 8 inch graphite disc situated 6 cm above the substrate. Sputtering was carried out with

RF power of 300 W and pure N₂ at a pressure of 17 mTorr. The substrate temperature during sputtering was held between 400 and 600°C. The graphite self bias was -1700V.

Exploratory C-N films were deposited by varying the sputtering parameters, e.g. the substrate temperature, sputtering gas, sputtering power, etc. Over twenty films deposited under various sputtering conditions were studied and the optimum process described above (referred to as the "standard process") was devised. We have also noticed that substrate heating reduces the deposition rate of the film but promotes crystallization. Therefore, a substrate temperature in the range of 400 to 600°C was selected in our standard procedure. Depending on the substrate temperature the deposition rate ranges from 0.1 to 0.5 μm/hour. The standard process was used to deposit C-N films (CN#23) on several substrates simultaneously, including (100) and (111) Si and (100) and (111) Ge wafers. The composition and thickness of the CN#23 film were studied by Rutherford backscattering spectrometry (RBS) using a 1.8 MeV ⁴He⁺ beam backscattered at 105° and 165° and proton resonant scattering (PRS) using a 1.55 MeV H⁺ beam. Details of the apparatus and the techniques have been published¹⁰. RBS and PRS results show that C-N films produced using this method have a nitrogen content ranging from 0 to 50%. Films deposited by the standard procedure, e.g. CN#23, are ~1μm thick with a nominal film composition of C_{0.6}N_{0.3}O_{0.1}. Fig. 1 shows the RBS spectrum of CN#23 on a Si substrate. RBS analysis also reveals that the film/substrate interface is abrupt with no apparent interdiffusion between the film and the substrate within the depth resolution of the technique (~200Å).

Scanning electron microscopy (SEM) studies on CN#23 show that the film morphology is rather smooth. Fig. 2 shows a crystalline particle of ~1μm size found in CN#23 on Si (100). This type of crystalline particle is difficult to find on the film and is more frequently found in regions where the overlayer C-N film peeled off. It is therefore suggested that these particles preferentially crystallize on the crystalline Si (100) surface and are buried by an amorphous C-N film. Energy dispersive x-ray analysis (EDX) shows

that the particles are composed primarily of C and N with a small amount of O. The N/C ratio of these particles are higher than the overall N/C ratio in the film. However, absolute quantitative determination of the composition of these particles is difficult due to the limitation of the electron beam size and substrate effects. The EDX results therefore suggest that the particle shown in Fig.2 is a N-rich crystalline C-N compound.

X-ray diffraction (XRD) measurements were carried out in a Siemens D500 X-ray diffractometer using a Cu anode. In order to increase the diffraction volume, a glancing incident angle of 1° was employed. XRD results in this glancing incident geometry on all of our films do not show any diffraction peak. This can be explained by the small atomic scattering factors of C and N in the particles; the relatively small amount of crystalline material present in the films, and the possibility that the crystalline particles may be textured with respect to the substrate Si so that the Bragg diffraction condition is not satisfied under a fixed incident angle. XRD analyses of the CN#23 film using the $(\theta-2\theta)$ Bragg geometry show many broad and sharp diffraction peaks. The broad peaks are believed to be from the amorphous graphitic phase in the film. Since the film is C-rich in composition, the presence of amorphous carbon phases is expected. Some of the strong diffraction peaks from the XRD spectrum of CN#23 do match the calculated β - C_3N_4 pattern. However, a similar diffraction pattern has also been observed for amorphous C or Si thin films on (100) Si substrate¹¹. These strong sharp peaks, therefore, can be attributed to substrate related diffraction. We believe that they are forbidden reflections for a perfect Si crystal, e.g. the (200) and (320) reflections, but become allowed due to stress induced by the presence of an overlayer on the substrate. Moreover, the strongest diffraction peak of the β - C_3N_4 phase, namely the (200) peak, is very close to the (200) peak of Si. Phase identification of the C_3N_4 crystal using XRD is therefore difficult unless a rather thick uniform layer of the material can be produced.

Transmission electron microscopy (TEM) investigations of the C-N films were performed using a Philips 301 microscope at an operating voltage of 100 kV. The

specimens were prepared by first mechanically grinding the samples into 3mm discs. The discs were then mounted faced down on a clear mica plate. The film surface was protected with wax. The specimen was backpolished from the substrate side in etching solution until a small hole was formed. A TEM dark field (DF) image of a plan-view specimen from CN#23 on Si (100) and its corresponding transmission electron diffraction (TED) pattern are shown in Fig. 3 a) and b), respectively. A section of both the {101} and {210} β - C_3N_4 diffraction rings was used for the dark field image shown in Fig 3a. The crystalline particles which we believe to be β - C_3N_4 grains shown in the DF image in Fig. 3a are ~ 0.5 μm in diameter and is observed on the edge of the hole in the specimen attached to the Si substrate. This is consistent with the SEM observation. These grains, which are distributed near the film/substrate interface embedded in the C-N polymeric matrix, are estimated to occupy less than 5% of the film volume.

The ring pattern in Fig. 3b indicates that the grains in Fig 3a are polycrystalline. Since the β - C_3N_4 grains are attached to the single crystal Si substrate, the ring pattern in Fig 3b overlaps with the {220} Si diffraction spot pattern. The lattice spacings are measured directly from the TED pattern and are tabulated in Table I. All the diffraction rings, with the exception of only a few rings with weak intensities, match with the theoretical β - C_3N_4 pattern. However, the lattice spacings as observed from TED are consistently smaller by a few percent than the calculated values for the theoretically predicted β - C_3N_4 . Using the strong (110) and (101) rings in the TED data, and assuming a hexagonal structure we calculated the lattice parameter of our observed crystalline phase to be $a=6.3\text{\AA}$ and $c=2.38\text{\AA}$. While these values are $\sim 2\%$ lower than the results from the total energy calculations ($a_0=6.43\text{\AA}$ and $c_0=2.46\text{\AA}$), the experimental and theoretical c_0/a_0 ratios are in good agreement. One possible reason for the slight reduction in the lattice parameters is that the crystals in our film may not have the perfect C_3N_4 composition. Moreover, the effect of the presence of a small amount of O (~ 5 -10%) in these particles may also play a role in the structure of the crystals and the absence of some diffraction

peaks in the TED pattern. The theoretical powder diffraction pattern calculated with the new shorter lattice parameters are presented in Table I in parentheses. A close match of the peak positions of the TED pattern with this new calculated pattern is observed. The rings which correspond to the β - C_3N_4 diffraction are indexed in Fig 3b.

In summary we have performed RBS, PRS, SEM, XRD and TEM measurements on C-N films deposited on Si and Ge wafers in the (100) and (111) orientations using RF diode sputtering. Small grains (~ 0.5 - $1\mu\text{m}$) are found in the film deposited on (100) Si. EDX, TEM and TED analyses show that these grains are N-rich as compared to the film and strongly suggest that they are the theoretically predicted β - C_3N_4 phase. The fact that these grains only grow on (100) Si suggests that these crystals bear a specific orientation relationship with the substrate. The samples we have studied deposited by the standard procedure are far from ideal. We believe that by further varying the sputtering parameters systematically C-N films with a much larger quantity of crystalline β - C_3N_4 particles can be produced.

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TABLE I Comparison of the TED data of CN#23 on Si (100) with the calculated β -C₃N₄ powder diffraction pattern.

TED		Calculated β -C ₃ N ₄ pattern ^b		
d (Å)	Intensity ^a	d (Å)	hkl	Intensity
		5.565 (5.46)	100	m
3.43(±0.05)	w			
3.15(±0.05)	m	3.213 (3.15)	110	m
2.65(±0.03)	vw	2.783 (2.73)	200	s
2.18(±0.02)	s	2.259 (2.18)	101	s
2.07(±0.02)	s	2.103 (2.06)	210	m
1.92(±0.02)	w	1.953 (1.90)	111	m
		1.855 (1.82)	300	m
1.76(±0.01)	w			
1.64(±0.01)	w			
1.56(±0.01)	vw	1.598 (1.56)	211	w
		1.543 (1.51)	310	w
		1.481 (1.45)	301	w
		1.345 (1.31)	221	w
1.25(±0.01)	s	1.277 (1.25)	320	w
1.17(±0.01)	vw	1.229 (1.19)	002	w
1.11(±0.01)	vw	1.133 (1.11)	321	m
		1.125 (1.09)	202	w
1.07(±0.01)	m	1.089 (1.06)	411	w

^a vs, s, m, w, and vw represent very strong, strong, medium, weak, and very weak diffraction intensities.

^b d spacings given in parenthesis are calculated values using the lattice parameters extracted from the TED data (see text).

Figure Captions

Figure 1 RBS spectrum of CN#23 film on Si. The detector is oriented at 105° with respect to the 1.8 MeV He ion beam. The maximum He backscattering energies for C, N and O are marked.

Figure 2 SEM micrograph of crystalline particles in CN#23/Si (100) sample. The composition of these particle is also measured by EDX to be N-rich.

Figure 3 (a) The transmission electron microscopy dark field image of the plan-view specimen from the CN#23 film on Si (100). (b) The corresponding electron diffraction pattern of the crystals shown in (a). The lattice spacings measured from the diffraction rings are tabulated in Table I. The diffraction rings corresponding to the β - C_3N_4 phase are also indexed in the Figure.

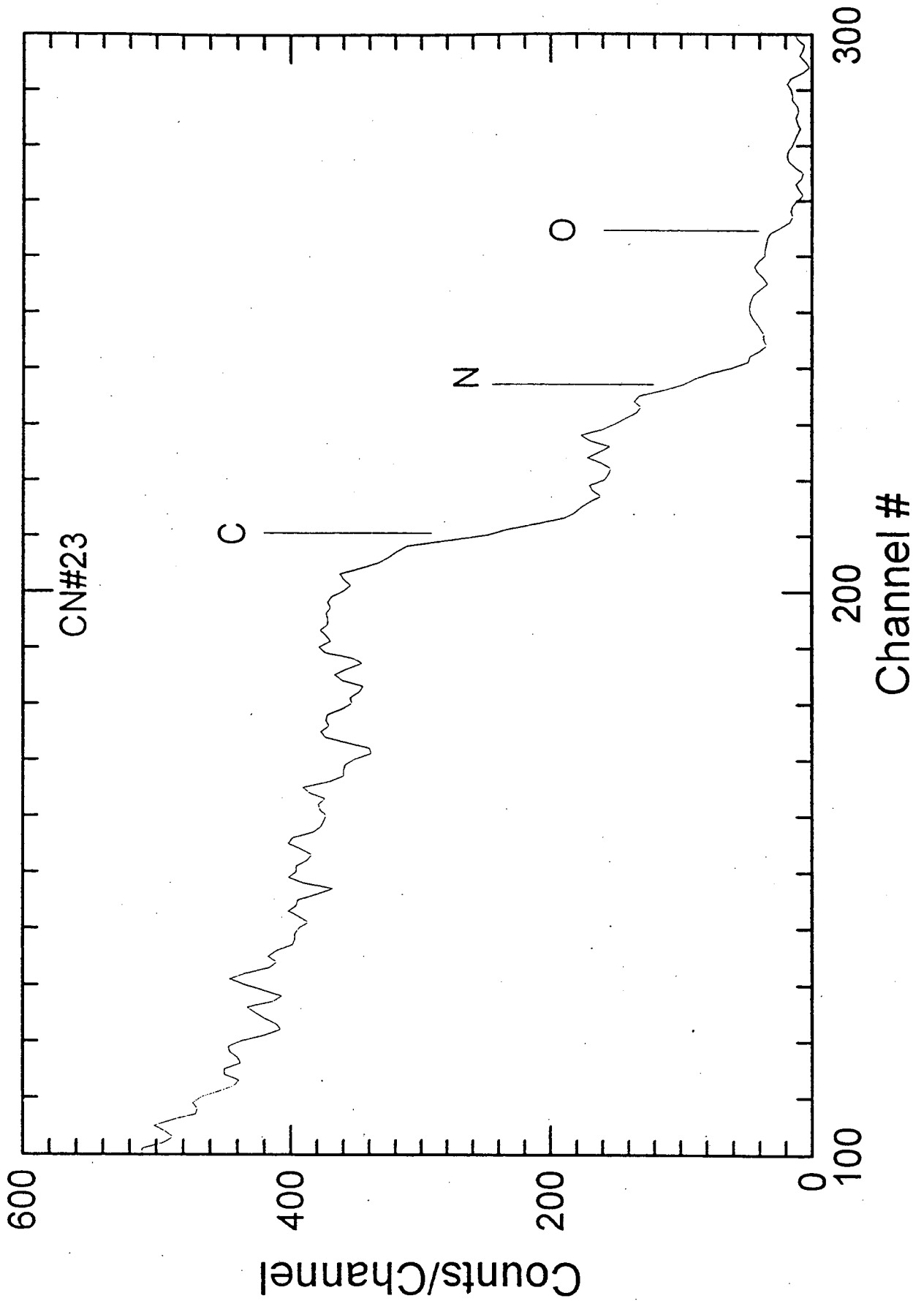
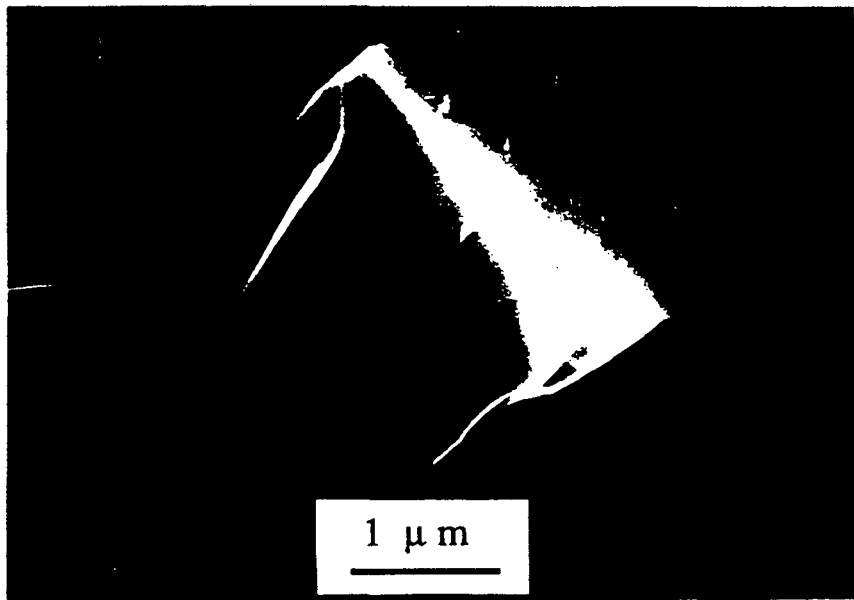


Figure 1.

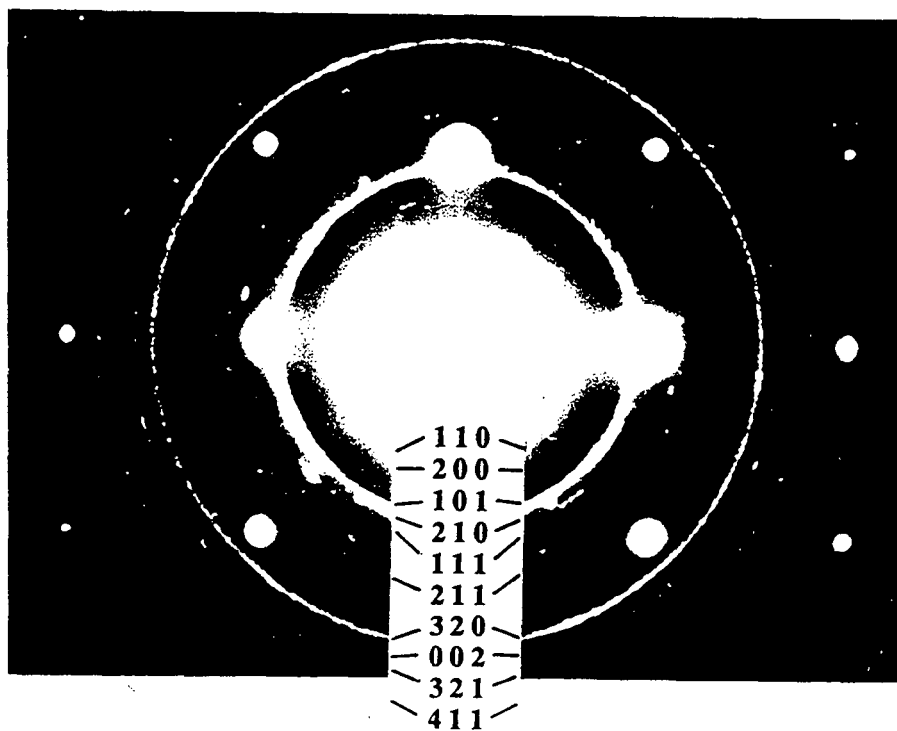


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Figure 2.



(a)



(b)

XBB 902-1023

Figure 3.

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