Appl. Phys. A 59, 83–86 (1994)

Applied Physics A Solids and Surfaces

Rapid Communication

Measurement of the elastic properties of evaporated C_{60} films by surface acoustic waves

H. Coufal[1], **K. Meyer**[1], **R.K. Grygier**[1], **M. de Vries**[1], **D. Jenrich**[2], **P. Hess**[2]

[1]IBM Research Division, Almaden Research Center, 650 Harry Road,
San Jose, CA 95120-6099, USA
(Fax: +1-408/927-2100, E-mail: COUFAl@almaden.bitnet)

[2]Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253,
D-69120 Heidelberg, Germany

Received 8 March 1994/ Accepted 19 May 1994

Abstract. Surface Acoustic Wave (SAW) pulses were excited in C_{60} films deposited on quartz and silicon substrates using pulses from excimer lasers with wavelengths of 248 nm and 308 nm for excitation. An optical beam-deflection technique and polymer electret transducers were utilized to detect the propagation of the SAW pulse with high spatial and temporal resolution, allowing an accuracy of better than 0.1% for SAW velocity measurments. With this technique the frequency dependence of the SAW velocity was determined for a number of fullerite films and density, as well as elastic bulk properties of the films were derived by a theoretical analysis of the dispersion effect.

PACS: 62.20.Dc, 62.65.+k

The availability of C_{60} as single crystals and thin films has stimulated the interest in the physical properties of this new class of van-der-Waals solids [1]. In addition to the well-studied optical and electrical properties, the mechanical properties are of fundamental interest for an understanding of the lattice dynamics of solid C_{60} (fullerite) materials [2-5]. Due to limited quantities of material, many of the classical mechanical methods are difficult to apply, or provide results with limited accuracy. For studies of the mechanical properties of thin films on a substrate, Surface Acoustic Waves (SAW) are the ideal tool [6]. In these waves the elastic energy is confined at the surface of the sample to a layer with a thickness of approximately one wavelength. With SAW pulses, excited for example by a suitable short laser pulse, the elastic properties of a thin film on a substrate can be determined simultaneously over a wide frequency range. If laser pulses of less than 20 ns duration are used for excitation, the bandwidth of the emitted SAW pulse is usually limited by the dimensions of the focus, and pulses with bandwidths exceeding 1 GHz can be generated. A ringing-free detection of transient SAW pulses with a bandwidth of up to 150 MHz is possible with a polymer electret foil transducer, which is pressed onto the surface [7, 8]. For detection with a higher bandwidth, an optical detection scheme was developed that relies on the deflection of a probe-laser beam by the transient SAW pulse [9]. Optical excitation and detection of SAW has, in addition to a bandwidth of 1 GHz, higher spatial resolution and requires no mechanical contact with the sample under study.

1. Experiment

In the present experiments SAW pulses were excited in the C_{60} films with laser pulses from excimer lasers. A conventional XeCl laser (Lambda Physik LPX105i) with a wavelength of 308 nm and a pulse duration of 20 ns and a KrF picosecond laser system (Lambda Physik PSL 400) with a pulse of 10 ps duration at a wavelength of 248 nm were used for excitation. For minimum width of the focus, the laser pulses were directed through a slit before passing through a cylindrical lens. According to micrographs of ablated samples, the focus was about $10 \div 20$ mm long and $20 \div 30$ μm wide. For pulse energies below 500 μJ, normally employed in these experiments, the acoustic pulses were generated predominantly by a thermoelastic mechanism, whereas at higher pulse energies, ablation of the C_{60} film was observed and contributed to nonlinear-signal generation.

Detection of SAW was accomplished by two different techniques. The first one used a 9 μm thick piezoelectric polymer film [poly (vinylidene) by Solyay] that is pressed against the sample under study by a knife edge with a width of approximately 45 μm resulting in a bandwidth of 150 MHz [7]. The signal is amplified by a Miteq AU-4A-0150 amplifier with a bandwidth of 500 MHz and recorded with a Tektronix digital storage oscilloscope TD 540 with an analog bandwidth of 500 MHz and a sampling rate of 1 Gs/s. With this experimental setup, very low laser pulse energies (<50μJ) and extensive signal averaging were employed. To take full advantage of the high bandwidth that laser generation of SAW affords, an optical probe technique has been developed [8]. A 20 mW diode laser with a wavelength of 691 nm is focussed onto the sample in an area of approximately 7 μm diameter. The reflected beam is divided by a reflecting knife edge into two beams which are detected by two Hamamatsu S4753 high-speed PIN diodes with a bandwidth of 1.5 GHz. Compared to a position-sensitive photodiode, this approach offers higher bandwidth and, compared to a standard knife-edge detection scheme, it offers a better signal-to-noise ratio. The difference signal of the two diodes is amplified by a Trontech W1G2K preamplifier with 1 GHz bandwidth and, when appropriate, a 2 GHz bandwidth Sonoma 330 amplifier was, in addition, employed. This signal is then recorded and averaged by a 1 GHz bandwidth Tektronix 7104 oscilloscope equipped with a Digital Camera System (DCS). The overall bandwidth of the detection system is 1 GHZ, and SAW rise times shorter than 1 ns were observed.

The velocity of SAWs was measured by determining the propagation time of the transient acoustic pulses along the surface for different distances between excitation laser-line focus and detector. This measurement of the arrival time of the SAW pulse eliminates concerns about nonlinearities of SAW propagation at the amplitudes that were employed in these experiments. The propagation distance of the order of several mm was measured using a micrometer with a precision of approximately 1 μm leading to a negligible error in the velocity. The experiments were performed on the (001)- and (111)-planes of silicon for different propagation directions and on fused-silica substrates. The silicon single crystals were intrinsic material with resistivities between 40 and 200 Ωcm. The surfaces were lapped and polished to a surface roughness of less than 2 nm rms. SAW velocities as a function of propagation direction on these crystals are reported elsewhere [9]. The polished quartz substrates (Heraeus Suprasil 3) had a comparable surface finish.

Fullerite films of thicknesses between 860 and 1300 nm were deposited on the substrates in a thermal evaporator at deposition rates between 2 and 18 nm/min from 99.9% pure C_{60}. C_{60} was prepared and purified with our standard procedure [9] or provided by commercial sources [11]. The purity of the material was verified with standard analytical techniques. The film thickness was determined with optical and conventional mechanical means; a quartz microbalance was utilized during the deposition process. SAW velocities were measured immediately after deposition and for an extended period of time after the deposition. Despite the fact that the optical appearance of the C_{60} film changed in the first hour after deposition, no change in the elastic properties was detectable, even after weeks.

2. Results

The laser-generated SAW pulses were detected optically or with the piezoelectric transducer at different distances from the laser-generated source. Optical detection was performed for distances from between 2 and 15 mm; piezoelectric detection was employed from 10 to 22 mm. At the longer distances SAW frequencies above 100 MHz are attenuated considerably. Attenuation and nonlinear effects that might occur at high sound intensities were observable but are not analyzed quantitatively in this paper.

From the observed time-dependent SAW signals, velocity and attenuation are derived by Fourier analysis of signals measured from at least two different distances away from the source. An example of a time-domain signal for a 860 nm thick C_{60} film on Si(111) with the SAW pulse propagating in the ⟨112⟩-direction and de-

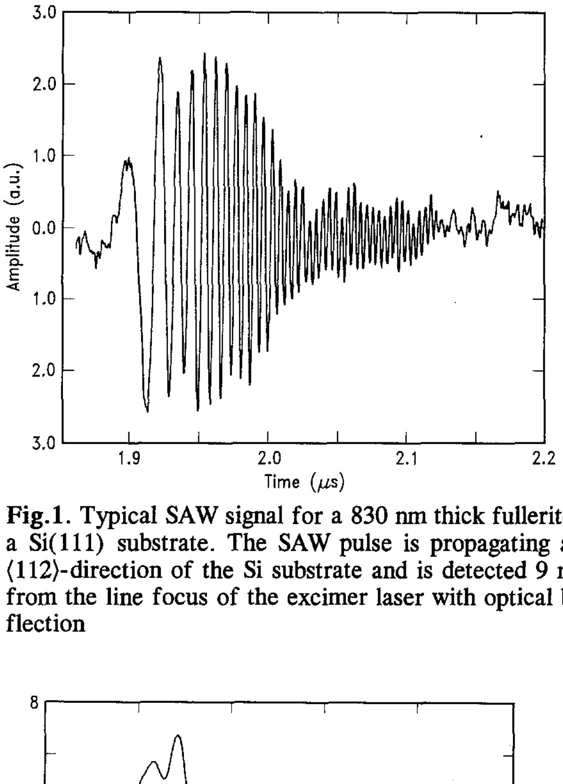

Fig.1. Typical SAW signal for a 830 nm thick fullerite film on a Si(111) substrate. The SAW pulse is propagating along the ⟨112⟩-direction of the Si substrate and is detected 9 mm away from the line focus of the excimer laser with optical beam deflection

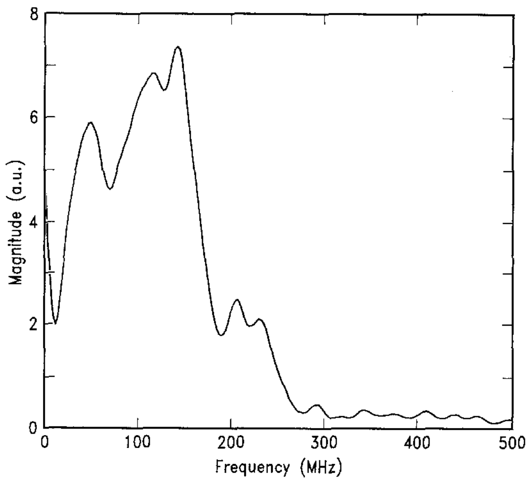

Fig.2. Fourier transformation of the time-domain signal shown in Fig.1

Table 1. The elastic properties of C_{60} films and crystals

	C_{60} film		C_{60} crystal
	On substr. (this work)	Free standing	
Density ρ [kg/m^3]	1660±10		1672 [3]
Young's modulus E [GPa]	12±1	45.4 [5] 81.7 [5]	15.9 [4]
Bulk modulus K [GPa]	6.4±0.5		14.4 [2] 18.1 [3]
Poisson's ration ν	0.18±0.04		
Velocity of sound transverse v_t [m/s]	1750±60		
Velocity of sound longitudinal v_l [m/s]	2820±80		
E/(1-ν) [GPa]	14.6±2	55.4 [5] 99.6 [5]	

tected 9 mm away from the laser-induced source by optical detection is shown in Fig.1; Figure 2 presents the corresponding Fourier transformation of this pulse. The virtual absence of signals above 300 MHz in the frequency-domain data is due to the strong attenuation of the SAW above 300 MHz. The frequency dependence of the phase velocity, also known as "dispersion effect", was fit with the Thierston model [12] to determine the density and the elastic constants of the film material. In the case of the anisotropic Si substrates it was necessary to solve the full 9×9 matrix instead of the reduced 4·4 matrix for isotropic substrates. By combining data from the experiments on different substrates and along different directions of the Si single-crystal substrates, a consistent set of parameters for the C_{60} films was derived. The errors shown in Table 1 reflect the sensitivity of the fit procedure and the sample-to-sample variations. In Fig.3 the SAW velocity as a function of frequency is shown for the same Si substrate covered with a 810 nm thick fullerite film that was used to record the time- and frequency-domain responses of Figs.1,2. The agreement between experimental data and the curve that is based on the parameters that are summarized in Table 1 is excellent; hardly any difference between experimental and fit curve is noticeable between 25 MHz and 250 MHz. In this frequency range the fit is sensitive to changes of any one of the parameters; below and above this frequency range numerical artifacts dominate the picture and do not contribute towards the interpretation of the data.

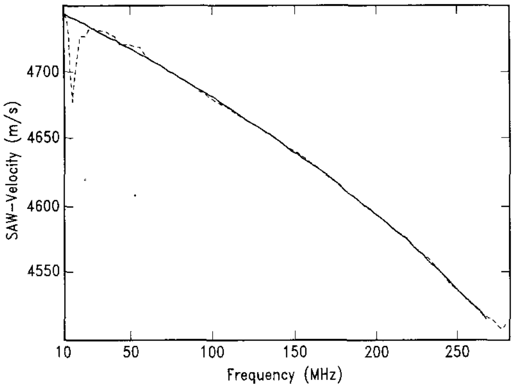

Fig.3. Frequency dependence of the SAW phase velocity derived from the SAW signal shown in Fig.1: —— experimental data; ----- numerical fit based on the parameters of Table 1

3. Discussion

In addition to the elastic properties that were derived from our experiments, Table 1 also summrizes data that were recently reported in the literature for C_{60} single crystals and free-standing films. To the best of our knowledge, our experiment is the first measurement of the elastic constants of fullerite films on a substrate. In addition, this method provides an accurate value of the density. Within the experimental error this density value is identical to that of C_{60} single crystals. This is rather unexpected since evaporated films typically have densities well below bulk samples of the same material due to numerous lattice defects in the film. One explanation for this surprisingly high density of the C_{60} films would be that the reported densities of C_{60} single crystals might be too low due to a small amount of low-density solvent, used during crystal growth, being trapped in the crystal.

A Young's modulus of 1210 GPa has been reported for diamond; values of 686 and 10 GPa are given for graphite, parallel and perpendicular to the slip planes, respectively [13]. This highlights the strong dependence of the elastic properties of carbon allotrops from the chemical bond between nearest-neighbor atoms. The elastic properties, e.g., the Young's modulus, of our C_{60} films are similar to the lower value for graphite. This is to be expected since van-der-Waals interaction is dominant between the individual molecular units of these two carbon allotrops.

The Young's modulus obtained for our fullerite films is, with 12 GAp, somewhat smaller than the value of 15.9 GPa recently reported for C_{60} crystals [4]. Using our value for the Posson's ratio, a Young's modulus of 45.4 and 81.7 GPa, respectively, can be derived from recent experiments on two free-standing C_{60} films [5]. These rather large differences indicate that the Young's modulus of C_{60} samples depends critically on the sample-preparation technique. Differences could be due to distortions and lattice defects in the structure of the films. It was also found that small concentrations of C_{70} decrease the elastic moduli of the film substantially.

Trapped solvent molecules would have the same effect. These explanations can be ruled out for our samples, however, due to the purity of the C_{60} material used and the deposition conditions.

Two values have been reported for the bulk modulus of C_{60} crystals, namely 14.4 GPa [2] and 18.1 GPa [3]. Both values are considerably larger than our result of 6.4 GPa for fullerite films. This highlights the fact that the fullerite films prepared at deposition rates of the order of several nm/min are, due to their disordered structure, substantially softer than the single crystals.

Acknowledgements. Support by IBM enabling P.H. to spend a sabbatical in San Jose is gratefully acknowledged.

References

1. W. Krätschmer, L.D. Lamb, K. Fostiropoulos, D. Huffman: Nature **347**, 354 (1990)
2. J.E. Fisher, P. Heiney, A. McGie, W. Romanow, A. Denenstein, J. McCauley, Jr., A.B. Smith: Science **252**, 1288 (1991)
3. S.J. Duclos, K. Brister, R.C.Haddon, A.R. Kortan, F.A. Thiel: Nature **351**, 380 (1991)
4. X.D. Shi, A.R. Kortan, J.M. Williams, A.M. Kini, B.M. Savall, P.M. Chaikin: Phys. Rev. Lett. **68**, 827 (1992)
5. C.B. Eom, A.F. Hebard, L.E. Trimble, G.K. Celler, R.C. Haddon: Science **259**, 1887 (1993)
6. A. Neubrand, P. Hess: J. Appl. Phys. **71**, 227 (1992)
7. A. Neubrand, P. Hess: Mater. Sci. Eng. A **122**, 33 (1989)
8. H. Coufal, R.K. Grygier, P. Hess, A. Neubrand: J. Acsoust. Soc. Am. **92**, 2980 (1992)
9. H. Coufal, K. Meyer, R.K. Grygier, P. Hess, A. Neubrand: J. Acoust. Soc. Am. (in press)
10. C. Yannoni, H.R. Wendt, M.S. de Vries, R.L. Siemens, J.R. Salem, J. Lyerla, R.D. Johnson, M. Hoinkis, M.S. Crowder, C.A. Brown, D.S. Bethune, L. Taylor, D. Nguyen, P. Jedrzejewski, H.C. Dorn: Synth. Met. **59**, 279 (1993)
11. Stefan Kaesdorf, Munich, Germany
12. H.F. Thiersten: J. Appl. Phys. **40**, 770 (1968)
13. A. Kelly: *Strong Solids* (Clarendon, Oxford 1973) p.10, p.263